



PROCESSES AND REACTIONS  
 Preparation of chloroprene. A. Khimich, I. Iva-  
 grad'ski and K. Chervachov. *Carbohydrate and Rubber*  
 (U. S. S. R.) 1937, No. 1, 31-4. Expts. on a lab. and  
 micro. scale were carried out to det. the optimum con-  
 ditions in the prepn. of chloroprene (I) by Carother's  
 method. The use of 2, 4, 6, 8 and 10 times the equiv.  
 amt. of HCl shortened the time of reaction to 1 hr. but  
 did not increase the yield of I; in some cases it even de-  
 creased it, and increased the yield of 2-butadiene, 2,4-  
 chloroprene (II). A concn. of HCl below 35% or above  
 37% at the start gave a lower yield of I, which reached  
 70% under optimum conditions. The optimum time of  
 reaction was 1 hr.; a shorter period decreased the yield,  
 and a longer period up to 6 hrs. did not increase it. The  
 optimum temp. at atm. pressure was 20-25°; a lower  
 temp. retarded the reactions and lowered the yield, and a  
 higher temp. led to the formation of II. The best results  
 were obtained from solns. of cyano and C<sub>4</sub>H<sub>6</sub>. The  
 optimum concn. of C<sub>4</sub>H<sub>6</sub> - C<sub>4</sub>H<sub>6</sub> - C<sub>4</sub>H<sub>6</sub> for the reaction was  
 15-20%.

AND 51.4 DETAILING LITERATURE CLASSIFICATION

FORM 51.4

FORM 51.4

FORM 51.4

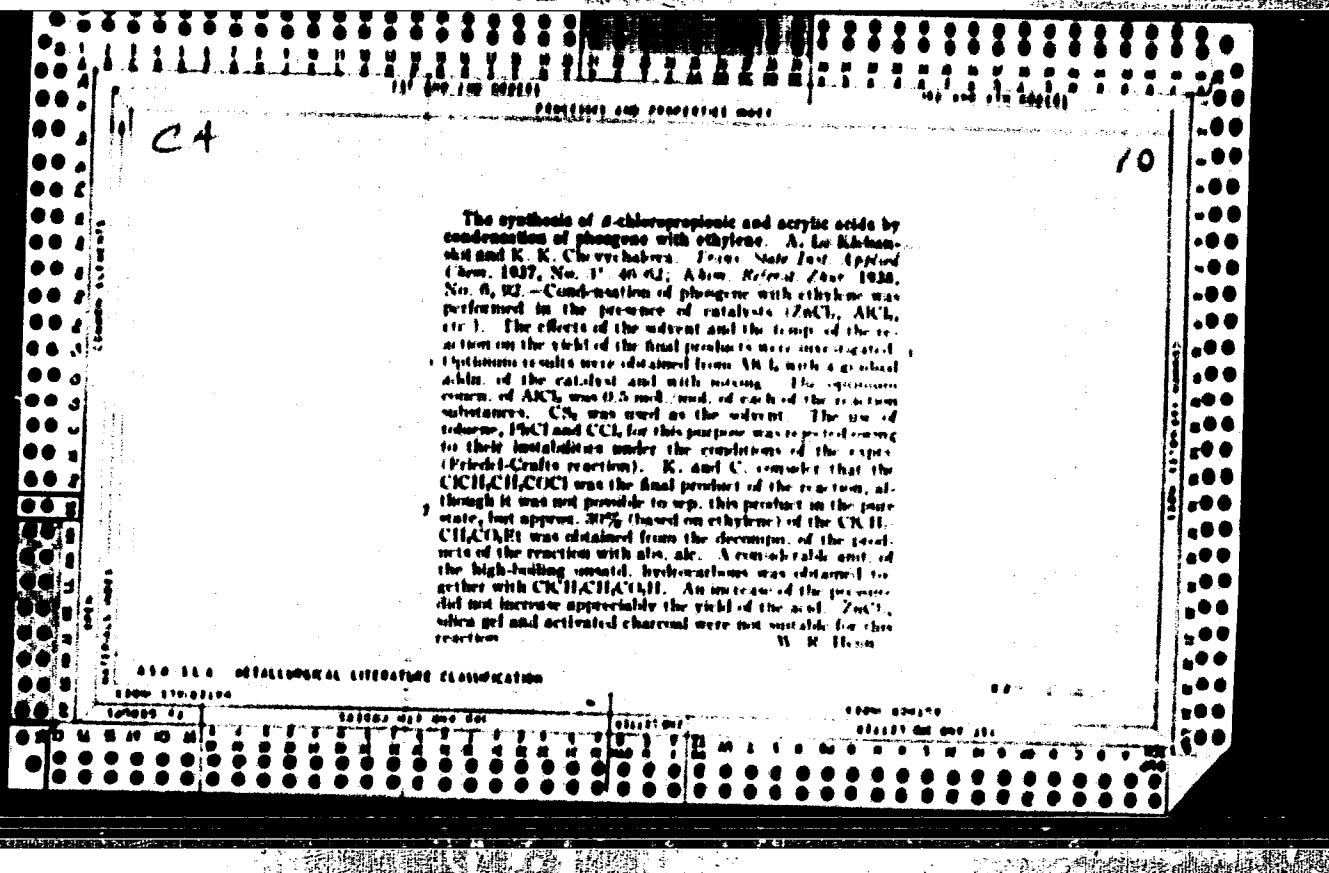
FORM 51.4

FORM 51.4

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100		<p>PROCESSING AND PROPERTY DATA</p> <p>Chloroprene polymers. II Determination of the unsaturation of chloroprene polymers. A. I. Kabanov and M. Mikhlin. J. Gen. Chem. (U.S.S.R.) 30:1280, 1959(1957); cf. C. A. 51, 2455. In the detn. of the amount of chloroprene rubber, the 1 mm. can be detd. about to the theoretical value by a modified Wism method of treating a sample with 10% excess of ICl in CCl<sub>4</sub> for 4 hrs. Since in the detn. of 1 value the chloroprene of chloroprene polymers is not hydrolyzed, the acidity found under the conditions of this method of detn. is caused by the substitution reaction, and should be deducted from the 1 values. Because of the variability of chloroprene and its sensitivity to atm. O<sub>2</sub>, it is not always possible to obtain consistent values for products of different origins.</p> <p>Chas. H. Hase</p>		<p>30</p>
<p>AND 51.4 DETAILING LITERATURE CLASSIFICATION</p>				

Investigation of the acids formed in the oxidation of the ester oil fraction of Zamba petroleum. A. I. Khiban-  
skii, I. M. Dolgopodskii and N. M. Shirokova. *Trudy  
Sov. Inst. Applied Chem.* (U. S. S. R.) No. 31, 23-45  
(1937); *Chem. Zvesti.* 1938, 1, 1247. The acids obtained  
by the oxidation of the ester oil in the air in the presence  
of Mn naphthosulfonate according to the method of G. I. Iversen  
show an acid no. of 110.2, sapon. no. 127.3, and 1 no.  
(Hohl) 11.4. It is not possible to dist. unsaponifiable  
matter by the method of Epie and Heng, as this method  
gives 80% unsaponifiable matter as against 30% by the  
method of Fabrian. The acids can be readily esterified  
with MeOH and HCl. Only 30-35% of the ester must  
be distilled off without decomposition at 3-5 mm. Hg;  
the major portion bps. 170-200°. Esters boiling within narrow  
limits cannot be obtained. The esters boiling to the  
naphthosulfonate acids are C<sub>11</sub>H<sub>22</sub>O<sub>4</sub> and C<sub>11</sub>H<sub>20</sub>O<sub>4</sub>. From esters  
boiling within fairly narrow limits acids having  
the simplest formulas C<sub>11</sub>H<sub>22</sub>O<sub>4</sub> and C<sub>11</sub>H<sub>20</sub>O<sub>4</sub> can be isolated.  
These can be converted into the ethanoic and the  
latter condensed with acetoacetic anhydride, but no esters  
obtainable. It is also impossible to obtain esters  
products by treating the acid anhydride with  $\beta$ -naphthol-  
naphthylchloride and with dibromomaleamic acid chloride.

M. G. Moore



# Synthesis from acetylene. A. L. Khrushch. Gos-

derst. Inst. Prikladn. Khim., Sverdlovsk 1910-59.

220 KJ (19.10); Khim. Referat. Zh. 1940, No. 4, 22.

Three reactions of  $C_2H_2$  were studied and each, processes in which these reactions were developed. (1)  $AcOH$  is produced from  $C_2H_2$  through  $AcCl$  which is obtained from the interaction of  $C_2H_2$  with a  $H_2SO_4$  soln. of  $HgSO_4$ . Optimum conditions of the reaction are: concn. of  $H_2SO_4$ , 20% (1.00 g. of  $Hg$ ) per (10 g. of the acid) and the temp.

70-80°. In the presence of  $Fe^{+++}$  salts in amts. of 1-1 and 2 with the  $Hg$  salt the hourly yield of  $AcOH$  increases 1.5 times. The duration of the activity of the  $Hg$  salt increases. The catalyst can be regenerated either electrolytically or by  $pptn$ .  $AcCl$  was oxidized to  $AcOH$  in the vapor phase in the presence of catalysts (acetates of  $Co$ ,  $Ni$ ,  $Mn$ ,  $V_2O_5$ ,  $Cr$ ,  $V_2O_5$ ,  $Fe$  and  $Cu$ ). Optimum results were obtained with the combination catalyst from the  $Co$  and  $Mn$  salts. Oxidation was carried out either with air or in vacuum. The yield was approx. 80%. Passing a mixt. of  $C_2H_2$  with water vapor over  $ZnO(V_2O_5)$  at the vanadate of  $Cu$  and  $Fe_2O_3$  at 400-500° produces as by-products approx. 17% of  $AcCl$  and 5% of  $AcOH$ . (2) Chlorinated org. solvents ( $C_2H_2Cl_2$ ,  $C_2H_2Cl_3$  and  $C_2H_2Cl_4$ ) were obtained by chlorinating  $C_2H_2$ . For obtaining  $C_2H_2Cl_2$ ,  $C_2H_2$  is chlorinated in the presence of  $Fe$  shavings, producing  $C_2H_2Cl_2$  from which a  $HCl$  soln. is split off during the reaction with milk of lime. To avoid

explosion the 1st step (production of  $C_2H_2Cl_2$ ) was carried out by mixing and by the triga method (mixing is preferable).  $C_2H_2Cl_2$  was obtained by chlorinating  $C_2H_2$  with a subsequent splitting off of  $HCl$  with milk of lime.  $C_2H_2Cl_2$  can be used as starting material for obtaining  $CH_3COOH$  by treating it with  $H_2SO_4$  at 140-150°. The continuous process for producing  $CH_3COOH$  was verified and optimum conditions for the reaction were obtained. The method produced excellent tech. and economical results. The app. used for the reaction must be made of acid-resistant alloys. (3) Synthetic rubber, sorprene, was obtained by polymerizing  $C_2H_2$ , producing vinylacetylene as the 1st product.  $HCl$  is added to vinyl-acetylene in the presence of a catalyst at a low temp. and the chloroprene is polymerized to rubber and stabilizer. Polychloroprene exists in several forms of which the  $\alpha$ -polymer (the linear structure corresponds to unvulcanized natural rubber) and the  $\beta$ -polymer (the latter structure corresponds to the soft vulcanizate of natural rubber) are of practical importance. The polychloroprene vulcanizate ( $\beta$ -polymer) is obtained by vulcanization of the  $\alpha$ -polymer. This vulcanizate (synthetic rubber) is superior in some respects to natural rubber. A method was developed for polymerizing chloroprene in an emulsion with the formation of the chloroprene latex which possesses excellent remaining properties for a range of further, such and other materials. Approx. 15% of divinylbenzene and higher polymers are obtained from polymerizing  $C_2H_2$ . The highest polymers can be further polymerized, producing lacquers. There are 3 types of polymers: liquid, gelatinous and solid polymers, differing in their degree of polymerization. Polymerization is carried out in a solvent in an atm. of an inert gas in the presence of stabilizers. In the presence of  $O$  the polymers produce easily exploding peroxide compounds. W. H. Brown

High-molecular-weight products of condensation of benzene with dichloroethane. A. L. Kabanov and G. I. Mironov. *J. Appl. Chem. (U.S.S.R.)* 14, 618-61 (in German, 651) (1941). --The authors studied the condensation of benzene and  $C_2H_5Cl_2$  by the Friedel-Crafts reaction to obtain polymeric products. Benzene was dried by  $CaCl_2$  and  $dist.$ . Before drying for  $C_2H_5Cl_2$ , was not sufficient, and it was found necessary to dry it over  $CaCl_2$  and  $dist.$ . A long series work with 5% of conc.  $H_2SO_4$  and  $dist.$ .  $C_2H_5Cl_2$  of expt. was run, using 15 g. benzene, 5 g.  $C_2H_5Cl_2$ , an av. temp. from 40° to 65°, and 15%  $AlCl_3$  (based on the benzene); the optimum temp. was found to be 45-50°. With the final temp. 70°, the reaction being completed in 3-4 hrs. Use of a lower temp. prolongs the reaction and the reaction, yielding a more crumbly product. It is necessary to stop the reaction by addn. of  $dist. HCl$  as a point when gel formation or swelling is observed; the mixt. is cooled simultaneously with the  $HCl$  addn. Failure to do this leads to a product of lower viscosity and plasticity. Variation of the  $C_2H_5Cl_2$  from 1.5 to 3 mols. to 1 mol. benzene showed that decrease of the amt. of  $C_2H_5Cl_2$  lengthens the reaction time and increases the plasticity of the product; 1.5 mol.  $C_2H_5Cl_2$  to 1 mol. benzene gave a crumbly product. The optimum ratio is 2.5 mols.  $C_2H_5Cl_2$  to 1 mol. benzene, giving a 90% yield of a plastic product. Variation of the  $AlCl_3$  from 10 to 30% (based on the benzene) showed that 15%  $AlCl_3$  allows completion of the reaction in 2.5 hrs. with a smooth reaction, 10%  $AlCl_3$  requires over 11 hrs. and only by addn. of further  $AlCl_3$ . It was impossible under the conditions used to

get a good recovery of the unused  $C_2H_5Cl_2$ ; hence recovery figures are not given. Good agitation is very important, especially near the end of the reaction when the product is very viscous. The working up of the product and the recovery of the  $AlCl_3$  complex are best done by treatment with  $NaOH$  and  $H_2O$ . The products obtained in this reaction were tested as addenda to chloroprene rubber; with a 1:2 mixt. the strength of the rubber was low, but plasticity and workability were improved. Plasticizers like tricresyl phosphate were tried in this formulation; the products were not apparently different from those without the plasticizer. The optimum conditions for this polycondensation were found to be: reaction temp., 55-65°;  $C_2H_5Cl_2$ -benzene ratio, 2.5:1; amt. of  $AlCl_3$ , 15% of benzene used; reaction time, 2-2.5 hrs.; final temp., 70°. The mixt. is treated with  $dist. HCl$ , the product ground with  $H_2O$ , the dichloride steam-distd. and the residue washed with  $H_2O$ ,  $NaOH$  and  $H_2O$ , and finally squeezed through rolls to remove considerable amt. of  $H_2O$ . It was found possible to use  $Al$  shavings pre-treated by a little  $HCl$  in the reaction mixt., instead of  $AlCl_3$ ;  $Cl$  may be used instead of  $HCl$ ; the reaction time is unchanged. Attempts to use  $Fe$  in a similar way failed, the use of  $FeCl_3$  is suggested but no work on this catalyst was done. It was noted, however, that if  $Al$  turnings treated with  $Cl$  are used as catalyst, there are several side reactions formation of appreciable  $PhCl$  and higher chlorides of benzene and ethane, even at 10-20°; the reaction products in this case are of inferior quality. It was found to be feasible to use  $HCl$  generated in one reaction batch for the prepn. of the  $AlCl_3$  catalyst from  $Al$  in another batch; likewise it was feasible to add small amt. of  $AlCl_3$  complex prepd. separately to a mixt. of  $Al$ , benzene and

2.  $\text{C}_6\text{H}_5\text{Al}$ , thus avoiding the time-consuming process of  $\text{AlCl}_3$   
 is also in its activity. Addition of 25% of this complex was  
 found to be sufficient to initiate the formation of  $\text{AlCl}_3$   
 from  $\text{Al}$ . It was found possible to preserve this catalyst  
 complex up to 5.5 days, if kept at low temp. In investiga-  
 tions of the product the latter was successively oxid. with  
 $\text{MnO}_2$ , petr. ether,  $\text{H}_2\text{O}$  and benzene. Only  $\text{MnO}_2$   
 and benzene effected any oxid. The  $\text{MnO}_2$  ext. was  
 found to contain  $(\text{C}_6\text{H}_5)_3\text{Al}$ , and a substance appearing to  
 be an oxidation product, approximating  $\text{C}_{10}\text{H}_8$ . Ben-  
 zene extn. yielded a red-brown plastic solid ( $\text{PnC}_{10}\text{H}_8$ ).  
 The elem. substance contained Cl, varying from 2.1% to  
 0.7% (3). The elem. residual product treated with  $\text{HNO}_3$   
 (red., as well as 1:1) at room temp. yielded a light-yellow  
 product, which was sol. into 2 fractions by treatment  
 with hot  $\text{H}_2\text{O}$ ; neither had a sharp m. p., dissolving above  
 200° with apparent decompos. Data. of  $\text{MnO}_2$  groups  
 showed the probability of its being a naphthalene acid,  
 on the basis of which the original reaction product was  
 probably a chain polymer with each  $\text{Pn}$  group being bound  
 to others through 2 aliphatic chains. (U. M. K.



Carboxy derivatives of butadiene. Their polymerization and the properties of the polymers. A. I. Kishinev and K. K. Chervachova. *J. Gen. Chem. (U.S.S.R.)* 10: 1101-14 (1940) (in Russian).—The poly- $\alpha$ -carboxybutadiene (I) was studied over  $H_2O$ - $BF_3$ - $SiO_2$  catalyst,  $BF_3$  being the main prod. A cyclic ether before was isolated, which was the dimerization product of I and fumaryl-butadiene (II). Polymerization rates for I and II derive were det. at 30, 40, and 50°; II polymerizes twice as fast as I. Doubling the temp. increases the polymerization rate by a factor of 2. Oxidation of the polymers gave succinic acid and acids of the corresponding esters, thus showing that the polymers have the structure type, 1,4-1,4 or 1,4-1,1. Vinylacetylene (III) could not be condensed with  $Ac_2O$  in the presence of the above catalyst; condensation with  $PClO_5$ , however, took place but the prod. could not be isolated in a pure state nor characterized. II; 6-oxo-1,4 or II with  $ac$ . alkyl gave polybutadienyl  $ac$ . (IV), which was sol. in water,  $HClO_4$ ,  $CHCl_3$ ,  $AcOH$ , and pyridine. A 25-100% range of III was passed into  $Ac_2O$  using 6-10%  $H_2O$ - $BF_3$ - $SiO_2$  with 5%  $Ac_2O$  being used as an activator; the reaction was carried out below 14°, the final temp. being 30° after a 2-4 hr. run; the product was isolated by extraction with  $H_2O$ , followed by washing with  $NaCl$  soln.,  $NaHCO_3$  and water, and drying; 1, by 50-60%  $BF_3$  1.411, d<sub>4</sub> 0.846, gives a maleic anhydride adduct, mp 100-71°. Use of  $CH_3$  or  $n$ -pr. ether for the initial reaction gave pure glides, while  $H_2O$  inhibited the reaction completely. The residues after iso-

lation of I gave, after fractionation, a product,  $\eta_{inh}$  1.38-0.5;  $n_D^{20}$  1.4478,  $d_4^{20}$  1.0682, which corresponds to a condensation of 2 mols. of I deriv. with hydrolysis of 1 acidic residue on the double bond and isomerization of the remaining alcoholic OH to a ketone; the product gave a carboxylic acid,  $\eta_{inh}$  1.08-0.5 (from water), while hydrolysis by 6.5 N HCl on a steam bath gave a diester, which was isolated as a monomeric ester,  $\eta_{inh}$  2.16-1.77; thus the product may be either a 1,2- or 1,4-isomer of *trans*-polyvinylcarbazole. A similar product,  $\eta_{inh}$  1.14-0.5,  $n_D^{20}$  1.4701,  $d_4^{20}$  1.041, was obtained from other residues in the prep. of II. Polymers of I or II deriv. were hydrolyzed by chemical means of 7-10% aq. NaOH, using PhMe for preliminary swelling of the polymers; hydrolysis was conducted at room temp. until the material formed a uniform sol., probably in an inert atm. and in the presence of an antioxidant; the sol. was then neutralized with HCl, the solvents were removed in vacuo, and the residue taken up in water and dialyzed; IV was occasionally obtained as a water-insol. yellow mass, in which case it was purified by multiple extr. in EtOH and water; it readily formed a polybenzoyl deriv. by treatment with excess  $SOCl_2$  in pyridine with heating 12 hr. on a steam bath; other sol. in  $CHCl_3$  and  $CCl_4$  with  $H_2SO_4$  it formed a brown powder, and in  $CHCl_3$  and PhEtMe, used in EtOH, PhEt,  $CCl_4$ ,  $CH_2Cl_2$ , ether.

**S. M. Kuntzeff**

Abstract derivatives of divinylacetylene. III. A. I. Kabanov, D. M. Krasnaya, and L. O. Gerasimov. *J. Gen. Chem. (U.S.S.R.)* 16, 1215-30 (1946) (in Russian); *J. Gen. Chem.* 1946, 1175-90. Divinylacetylene (I) (17.5 g.) in 75 g. abs. EtOH contg. 11.75 g. KOH was refluxed 40 hrs.; the excess KOH removed by  $\text{CO}_2$ , and the org. layer dried, to give 1-ethoxy-2,3,5-hexatriene, bp 55-57°,  $n_D^{20}$  1.4041,  $d_4^{20}$  0.8082. Chlorination of the triene at -30° in  $\text{CHCl}_3$  with 1 mol.  $\text{Cl}_2$  gave a mixt. of di- and tri- $\text{Cl}$  derivs. which were not well separable and bp 54-170°. The triene was polymerized in the presence of oxidizing agents,  $\text{TiCl}_4$ ,  $\text{ZnCl}_2$ , or  $\text{AlCl}_3$ ; the polymerization was turbulent at 60° and fairly rapid at 100°, although the polymers were not homogeneous and were mixts. of condensed and liquid masses. Condensation of I with MeOH, using MeONa as catalyst, failed to give more than a trace of the MeONa deriv., even after 12 hrs. at 100° (sealed tube); however, heating 40-60 hrs., without access to air, with either abs. KOH or MeONa, resulted in 12-13% 3-ethoxy-1,3,5-hexatriene, bp 70-8°,  $n_D^{20}$  1.4078,  $d_4^{20}$  0.8077. Attempts to condense I with  $\text{HCOOH}$  and  $\text{AcOH}$ , using  $\text{BF}_3$  catalyst, resulted in tar formation. Addn. of I to 40 g. MeOH, contg. 1.6 g.  $\text{H}_2\text{O}$ , 0.1114 g.  $\text{ClCCO}_2\text{H}$ , and 0.5 cc.  $\text{BF}_3$ , followed by stirring 21 hrs., gave 11.2 g. di- $\text{Cl}$  deriv., bp 55-6°,  $n_D^{20}$  1.430,  $d_4^{20}$  0.8082, which was not characterized further. IV. Chloroethoxy derivatives of divinylacetylene. 1946, 1231-42. When 50 g. divinylacetylene (I) and 40 g.  $\text{Cl}_2$  are simultaneously added to 250 g. 18.4% aq. KOH during 8 hrs. at -16° to 5°, there is formed a mixt. of chlorination and chloroethoxy products, bp 15-100°, which could not be adequately purified by distn. Repeated distn. gave fairly pure product, bp 60-8°,  $n_D^{20}$  1.404,  $d_4^{20}$  1.0025. The pure  $\text{C}_6\text{H}_9\text{OCl}$ , bp 60-8°,  $n_D^{20}$  1.404,  $d_4^{20}$  1.0025. The pure product was best obtained by the following method:  $\text{HNO}_3$  prep. according to Sandmeyer (Ber. 19, 227 (1886)), was led into a soln. of I in  $\text{CCl}_4$  at 5-15°; the

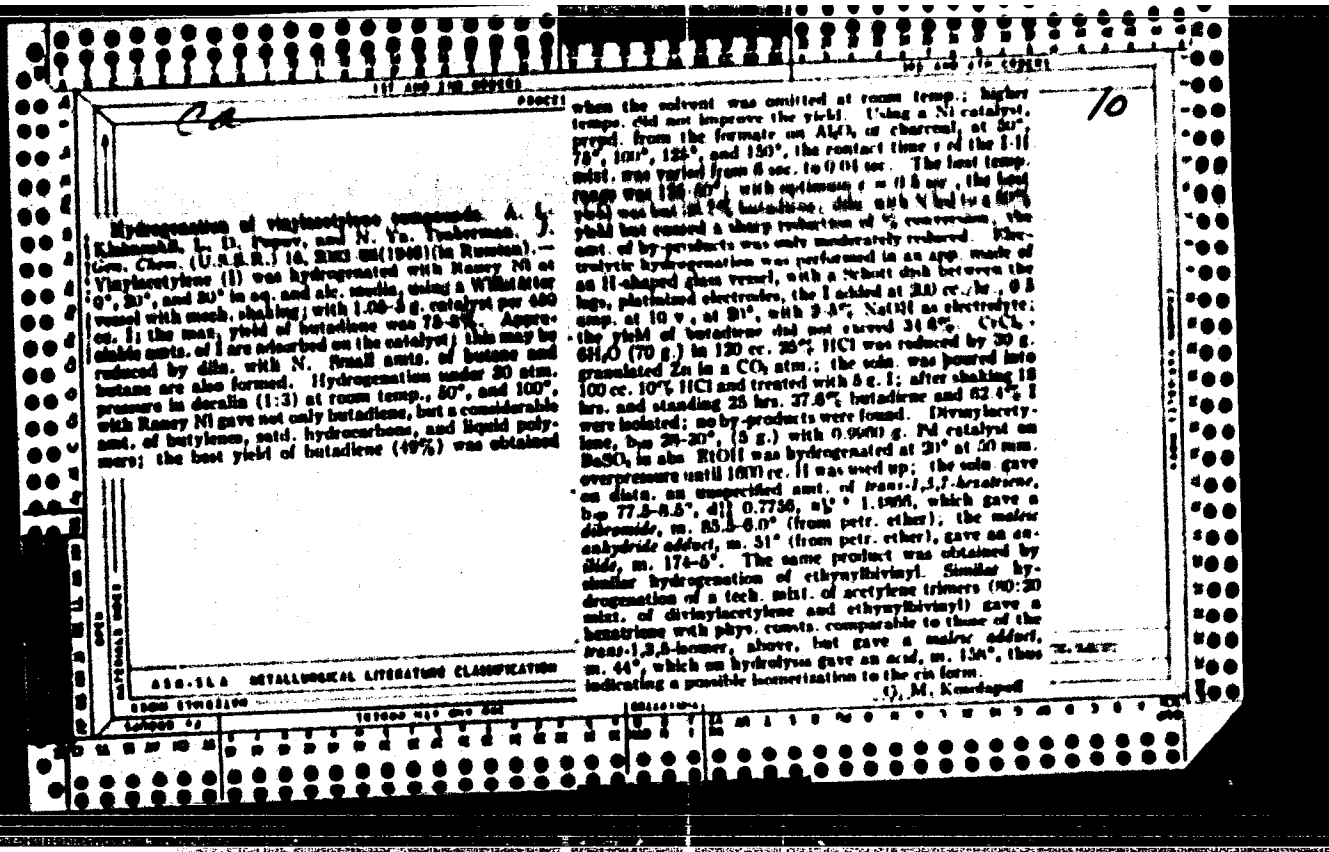
mixt. was allowed to stand several hrs. at room temp., heated 1-2 hrs. to 100°, and distd. to give the chloroethoxy deriv. (II) of I, bp. 60-1°,  $n_D^{20}$  1.4041,  $d_4^{20}$  1.0125, with the  $\text{EtO}$  and  $\text{Cl}$  shown to be located at the 1,3-positions (although the exact assignment of each was not done) on the basis of  $\text{KMnO}_4$  oxidation studies. When II was treated with 10% aq. KOH at room temp. in the dark 4 days, there was formed a very readily oxidizable product,  $\text{C}_6\text{H}_9\text{O}$ , apparently 1(7)-ethoxydivinylacetylene, bp 60-65°,  $n_D^{20}$  1.3977,  $d_4^{20}$  0.8113. II polymerizes slowly on heating 40 days at 60° without a catalyst to the extent of 60%; addn. of  $\text{TiCl}_4$ ,  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ , or oxidized turpentine accelerates the polymerization only moderately; the temp. effect on the polymerization, however, is very great, for at 100° 82% polymer forms in but 57 hrs. The polymers are solids which are sol. in chlorinated solvents.

O. M. Krasnaya

MELETSKY, A. I.

"Chloroethoxy-Derivatives of Divinylacetylene. IV " by A. I. Meletsky, D. M. Krasinskaya, and I. G. Safonova. (p. 1241)

SO: Journal of General Chemistry (.Zhurnal Obshchei Khimii) 1961, Volume 16, No. 8

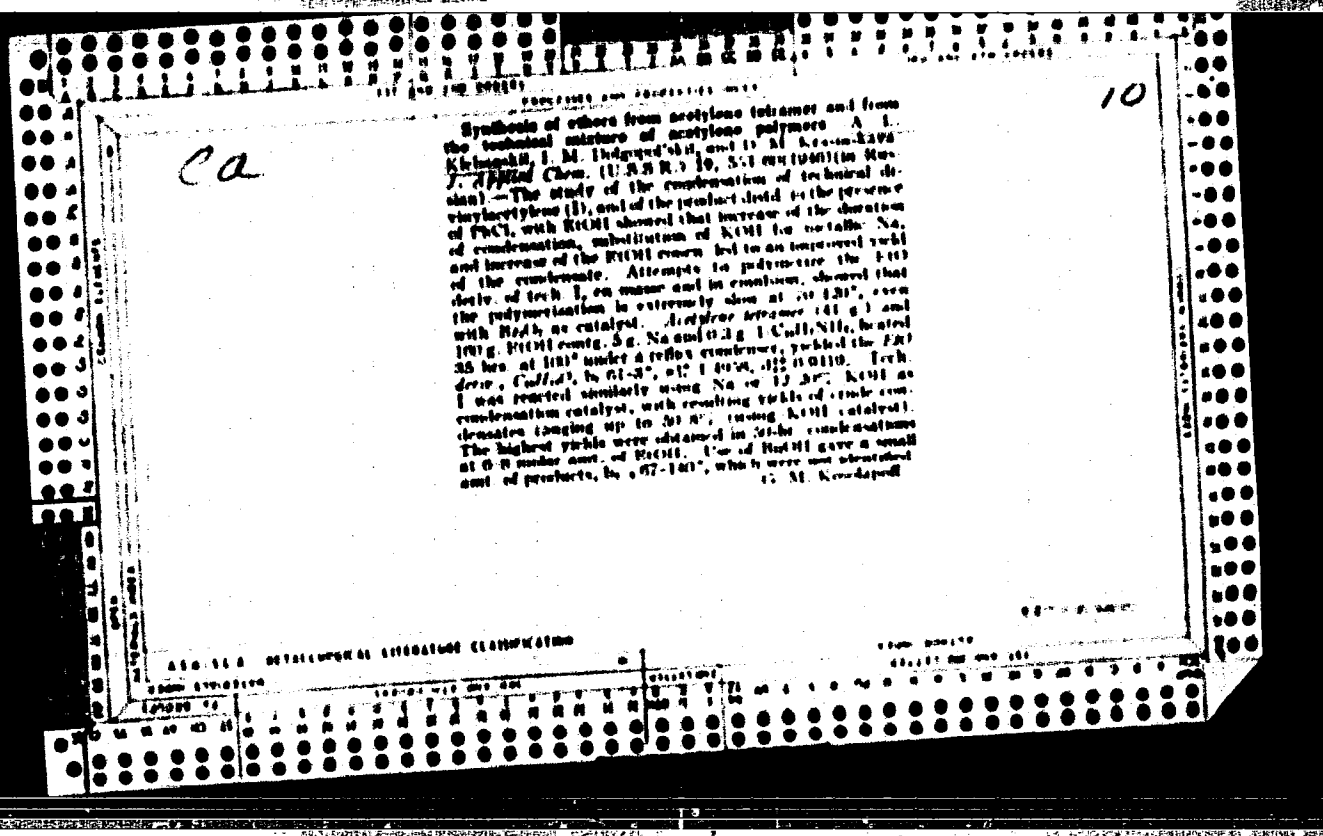




KLEBANSKIY, A. L.

Synthesis of the butyl ethers of divinylacetylene. V. A. L. Klebanski, I. M. Dogopolskii, and D. M. Krasiuskaya. J. Applied Chem. (U.S.S.R.) 19 286 92 (1946)- The object of this work is the elaboration of methods of obtaining divinylacetylene derivs. capable of polymerizing with the formation of film-forming substances which would be of greater tech. importance than the divinylacetylene polymer. A table is given of the 6 theoretically possible Bu ethers of divinylacetylene, namely,  $\text{CH}_3\text{CH}:\text{C}:\text{CHCH}_2\text{OC}_4\text{H}_9$  (1 6 isomer),  $\text{CH}_3:\text{CHCH}:\text{C}-(\text{OC}_4\text{H}_9)\text{CH}:\text{CH}_2$  (3-4),  $\text{CH}_3\text{CH}:\text{C}:\text{C}(\text{OC}_4\text{H}_9)\text{CH}:\text{CH}_2$  (1-4),  $\text{C}_4\text{H}_9\text{OCH}_2\text{CH}:\text{C}:\text{CHCH}:\text{CH}_2$  (4-1),  $\text{CH}_3\text{CH}(\text{OC}_4\text{H}_9)\text{C}:\text{CCH}:\text{CH}_2$  (4-2), and  $\text{C}_4\text{H}_9\text{OCH}_2\text{CH}_2\text{C}:\text{CCH}:\text{CH}_2$  (2-1). Structure was studied by oxidation; oxidation with  $\text{KMnO}_4$  showed that the 1 4, 4 1, 3 1, and 1 6 derivs. were important.

A. E. Karr



KLEBANSKIY, A. L.

PA 15T38

USSR/Chemistry - Butadiene  
Chemistry - Bromobutadienes

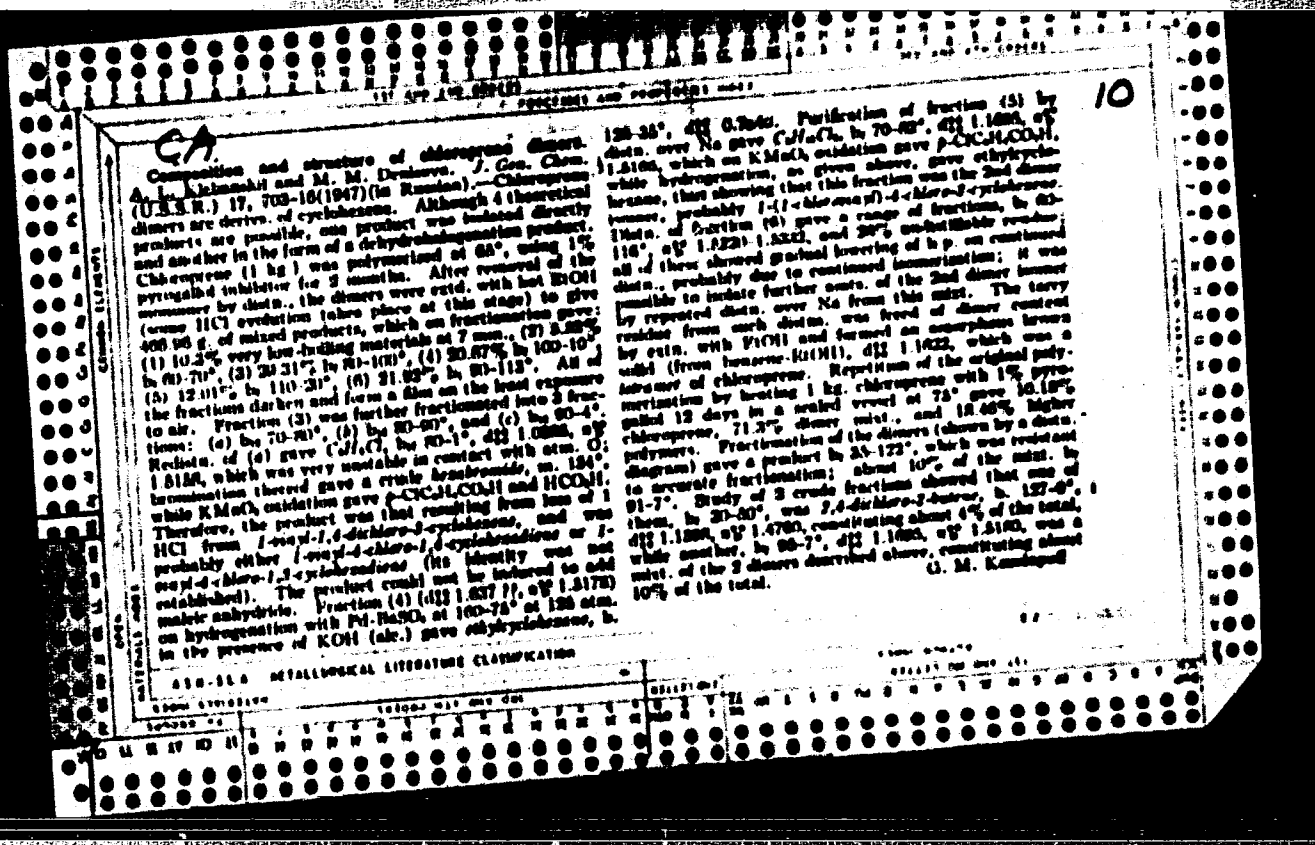
Feb 1947

"Splitting Off of Hydrogen Halides from the  
Dihalogen Butenes Formed During the Chlorination  
and Bromination of Butadiene: Synthesis of Alpha-  
chlor- and Alpha-bromobutadienes, Their Character-  
istics and Properties of Products," A. L. Klebanskiy,  
R. M. Sorokina, Z. Ya. Khavin, 16 pp

"Zhur Obshch Khim" Vol XVII, No 2 - p. 251-

15T38





Structure of polychloroprene as determined by osmotic pressure. II. A. Kabanov and K. Chervinskaya. J. Gen. Chem. (U.S.S.R.) 17, 941-95(1947); cf. C.A. 31, 6021. Five chloroprene (I) polymers were prep. as follows: (1) I was polymerized in the presence of a regulator (not described) at 40°. Polymerization was stopped at a yield of 14%. The polymer was sol. in  $\text{CHCl}_3$ . (2) Random polymerization of I was carried out in the presence of antioxidants. The polymer yield was limited to 60% so that  $\text{CHCl}_3$ -sol. polymer was obtained. (3) A latex was made by Cvetkov's method (C.A. 26, 76) which involved polymerization of an emulsion of I in a 2% aq. soln. of Na oleate. (4) I was placed in a sealed tube and heated at 80° for 1 hr. The polymer yield was 87%. (5) Liquid I polymer was made by an industrial polymerization process involving the use of regulators, but not otherwise described. Each of the 5 polymers was subjected to osmotic pressure by dissolving it in  $\text{CHCl}_3$  and bubbling  $\text{O}_2$  into the soln. until the mnt. lost its capacity to react with  $\text{Br}_2$ . The osmotic pressure was determined with aq.  $\text{H}_2\text{O}_2$  and the products analyzed. In every case 87% or more of the hydrocarbon skeleton could be identified as succinic acid (II),  $\text{HCOOH}$ , or  $\text{CO}_2$  in the final mnt. (4 these 5 products, II represented approx. 90% in every case. This result indicated that all 5 polymers were 1,4-addn. polymers of I. The percentage of the hydrocarbon skeleton identified was lowest in the polymers made by methods (3) and (5), i.e., 86-88%, compared to 90-96% for the other 3 polymers. The product from method (3) was believed to contain an appreciable amount of polymer and also oxidizing agents and the like that did not respond in the normal way to osmotic pressure. The liquid polymer was thought to have given low results because of the presence of unoxidized reaction products between the polymer and the regulator. Expts. were also carried out in which the osmotic pressure was determined with  $\text{HCl}$  in aq. soln.

with or without II orthoformate. The products were not completely identified but contained II succinate, the osmotic pressure of II, and a fraction with a composition corresponding to analysis and mol. wt. to impure  $\text{C}_4\text{H}_6\text{O}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$  dimer, possibly representing a unit of the monomer and trimer of this compound. No derivatives of II dihydroxydicarboxylic acids were identified, although an intensive search was carried out for the detection of this compound. The rate of the reactivity with  $\text{Br}_2$  as an index for deg. the consumption of osmotic pressure was investigated critically. The consumption of  $\text{Br}_2$  was approx. constant up to the end of sharply. It was observed that  $\text{Br}_2$  tended to react with the osmotic pressure unit, by substitution, since  $\text{HBr}$  was evolved in aq. soln. as large as 32% of the total  $\text{Br}_2$ .

H. K. Livingston



KLEBANSKIY, A. L.

**Mechanism of the hydration of acetylene.** A. L. Klebanskiy and V. D. Titov. *J. Applied Chem. (U.S.S.R.)* 20, 1115-12 (1947) (in Russian).—In analogy with Ipatiev's scheme (*C.A.* 29, 7017) of the polymerization of olefins in the presence of strong acids, formation of MeCHO from  $C_2H_2$  in acid soln. is assumed to proceed over intermediate, readily hydrolyzable, vinyl esters of the corresponding inorg. acid, e.g.,  $H_2PO_4$ . Without catalysts, yields of MeCHO are poor; thus,  $C_2H_2$  passed through 80%  $H_2PO_4$  at 150° gave only 2% MeCHO. The role of heavy metal salt catalysts is attributed in the main to an increase of the soly. of  $C_2H_2$  through formation of complex compds. of  $C_2H_2$  and the metal salt, and to activation of the  $C_2H_2$  owing to ionization of an H atom of  $C_2H_2$ . Effective catalysts are, besides Hg, salts of Zn, Cd, and particularly Cu and Ag. In the liquid phase, in strong acid soln., polymerization predominates over formation of MeCHO; with  $C_2H_2$  dil.

with  $N_2$  in the ratio 1:2, at 150°, with  $Cu_2O$  dissolved in 70%  $H_2PO_4$ , the  $C_2H_2$  reacted in one run to the extent of 70% (as against 20% without  $Cu_2O$ ) with a yield of 7% MeCHO. Polymerization is reduced considerably, and the yield of MeCHO increased, in the gas phase; at 350°, on 50%  $H_2PO_4$  on a solid carrier, the yield of MeCHO in a single run was 30% with respect to the  $C_2H_2$  passed, 60-70% with respect to the  $C_2H_2$  reacted. With a catalyst of  $H_2PO_4$  and a mixt. of Zn and Ag or Cu salts on a solid carrier (carbon or silica gel), at 275-350°, with  $C_2H_2$  dil. with  $H_2O$  or in the vol. ratio 1:10 and with  $N_2$  in the ratio 1:2 (gas mixt. contg. 5 vol. %  $C_2H_2$ ), the av. yield of MeCHO is 60% with respect to the  $C_2H_2$  passed, and 92-95% with respect to the  $C_2H_2$  reacted. This catalyst produced 330 g. MeCHO/hr./l. catalyst at a contact time of 0.2 sec.

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31

The structure of polymers of 2,3-dichloro-1,3-butadiene and 1,2,3-trichloro-1,3-butadiene. A. L. Kabanov and K. K. Chervinskaya. *Zhur. Obshch. Khim.* (Gen. Chem.) 20, 1102 (1950). The polymer of 2,3-dichlorobutadiene is an isotactic, melt solid, the product is crumbly when prepolymerized in emulsion or in  $CCl_4$  solution. Thermal analysis in  $CHCl_3$  suspension gave 187°,  $CHCl_3$ , 81°,  $HCl$ , 11, and 42.75% succinic acid, which indicates that some 1,2-polymerization takes place along with the more common 1,4-reaction. The polymer of the 1,2,3-trichloro analog is also insoluble in  $CHCl_3$  (except for very early stages of polymerization); its osmolytic indicated fully normal 1,4-structure for the early polymers (80% completion), while completed polymers must contain some branched 1,2-reaction products, as shown by its study. The org. acid isolated was fumaric, identified as such and as its Ag salt. G. M. Koshopoff

KLEBANSKIY, A.L.

~~ALL INFORMATION CONTAINED HEREIN IS UNCLASSIFIED~~

**Fifth yields the mechanism, again according to mechanism, the rate of thermal decomposition of the disulfide is smaller than that of tetrasulfine. Radical decomposition of tetrasulfine in CCl<sub>4</sub> at 145° gives liquid SCl<sub>2</sub> in the product formed when the radical S<sub>2</sub>Cl<sub>2</sub> is formed. The product is also formed in the decomposition of tetrasulfine in CCl<sub>4</sub> at 145° and in the decomposition of tetrasulfine in CCl<sub>4</sub> at 145°.**

KLEBANSKIY, A. L.

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Synthesis of a series of derivatives based on 2,4-dichloro-  
butene-2. Synthesis and properties of 2-chloro-2-butene-4  
Klebskiy and L. E. Eganov. Zashch. 1958  
No. 1, p. 19. (Chem. Abstr. 52:12,426)  
The authors describe the synthesis of 2-chloro-2-butene-4  
from 2,4-dichlorobutene-2 and 20% NaOH and its properties.  
2-chloro-2-butene-4 (bp 48.5°C) was obtained in 85% yield.  
A lower content of NaOH gave a lower yield.  
The authors also describe the synthesis of 2,4-dichlorobutene-2  
from 2-chloro-2-butene-4 and 20% NaOH in the dark with  
the addition of a catalyst. The results are as follows:  
1. The best yield is obtained with 20% NaOH.  
2. The catalyst  $CaH_2$  formed from RSH and excess  $H_2$   
in  $Et_2O$ . Heating the solid with  $Hg(CN)_2$  in  $Et_2O$  gave a  
floculent colorless  $Hg$  salt, decamp. 100°C, which was not  
analyzed. RSH with  $Pb(OAc)_2$  gave the Pb salt, yellow  
amorphous mass. RSH and  $Cu_2O \cdot NaOAc$  gave the Cu  
salt,  $Cu_2(CN)_2$ , yellow amorphous, 44, decamp. about  
100°C, unstable in storage.

USSR/Organic Chemistry. Synthetic Organic Chemistry. E-2

Abs Jour : Ref Zhur - Khimiya, No. 8, 1957, 26722.

Author : Klebanskiy, A.L.; Markin, V.V.,  
Chevychalova, K.K.

Inst :  
Title : Synthesis of Basis of 2,4-Dichlorobutene-2.  
Synthesis of Cyanamide Derivative, Binary  
Amine and Its Derivatives.

Orig Pub : Zh. obshch. khimii, 1956, 26, No. 9, 2433 -  
2435.

Abstract : The interaction between 2,4-dichlorobutene-  
2 (I) and  $\text{CaNCN}$  (II) in presence of an equi-  
valent amount of  $\text{NaOH}$  results in the formation  
of di-(2-chlorobutene-2)-cyanamide (III), the  
following hydrolysis thereof produces di-(2-  
chlorobutene-2)-amine (IV). 155 g of I in

Card 1/3



KLEBANSKY, A. L. Klebansky, A. L.

2  
 1. Mechanism of the reaction of methyl chloride and silicon in the presence of copper. A. L. Klebansky and V. L. Fikhtengolts. Zh. Obshchei Khim. 26, 2002 (1956). The literature on the mechanism of formation of silanes from  $HX$  and  $Si$  was reviewed. Examined by x-rays of the  $Si-Cu$  reactant formed either by fusing, pressing, and heating under  $H_2$  or pressing and heating  $Si-CuCl_2$  with discs of  $SiCl_4$ , and by deposition of  $Cu$  on  $Si$ , showed that the reactant is an intermetallic compound of  $Si$  and  $Cu$ . Elevation of operating temp. increases the yields of  $MeSiCl_3$  and gaseous products, with decrease in that of  $Me_2SiCl_2$ . If the reaction is run in the presence of dry  $HCl$ , the yield of  $MeSiCl_3$  rises significantly, while

addn. of  $Mg$  lowers the yield. These results are produced by the donation or acceptance, respectively, by these additions of  $Cl$  to or from the reacting mass of  $Si-Cu$ . The formation of gaseous products can be attributed to dissociation of  $MeCl$  and pyrolysis of the  $Me$  groups. Passage of  $MeCl$  over reduced  $Cu$  caused transfer of  $Cl$  to  $Cu$  with formation of  $C$  and gaseous products which are very prominent at about  $400^\circ$ . Formation of  $MeSiHCl_2$  and related materials is caused by reduction by atomic  $H$  formed in pyrolysis of  $Me$  groups. With  $HCl$ , which pyrolyzes more readily than  $MeCl$ , the yield of gaseous products increases considerably. When  $HCl$  is passed over the  $Si-Cu$  mass there is formed  $SiCl_4$  accompanied by much  $H_2SiCl_2$  and some  $H_2$ . The catalytic role of  $Cu$  in the reaction is attributed to increased polarization of the  $C-Cl$  bond by the positive charges of the  $Cu$  atoms of the intermetallic compound of  $Si-Cu$ . (U. S. Koshlyakov)

KLEBANSKIY, A. L.

1341. Function of polymer and thiol in the  
polymerization of chloroacetaldehyde and the crosslinking  
of polymers

1342. The role of the polymer in the  
polymerization of chloroacetaldehyde and the crosslinking  
of polymers

A. L. Klebanskiy  
Institute of Synthetic Rubber Research  
Academy of Sciences, Leningrad

KLEBANSKIY, A. L., and TSURUTSUKI, H. Y.

"Copolymerization of sulfur and chloroprene," a paper presented at the  
9th Congress on the Chemistry and Physics of High Polymers, 20 Jan-2 Feb 57,  
Moscow, Rubber Research Inst.

B-3,004,395

Summary of operations - [illegible]  
[illegible]  
[illegible]  
[illegible]

Distr: 47213

Synthesis of *N*-mono- and *N,N*-dialkyl derivatives of hexamethylenediamine / A. L. Klebanov and M. S. Vlasova. *Russ. Chem. Revs.* 1957, 26, 11957. *N*-mono- and *N,N*-dialkyl derivs. of hexamethylenediamine (I) with radicals of different chain lengths and structure were prepd. by alkylating with aldehydes and ketones and reducing at 10-20° and 80-100 atm. pressure in EtOH with Pt-black or Raney Ni. The derivs. of I prepd. were (yield, b.p.,  $n_D^{20}$ ,  $d_4^{20}$  and the alkylating agent given): *N,N*-di-Et, 41%, b.p. 101-5°, 1.4440, 0.821, AcH; *N,N*-di-Pr, 68%, b.p. 102-5°, 1.4481, 0.831, propionaldehyde; *N,N*-di-Bu, 87%, b.p. 131-3°, 1.4479, 0.823, butyraldehyde; *N,N*-di-*n*-pentyl, 85%, b.p. 112-15°, 1.449, 0.818, *n*-butyraldehyde; *N,N*-diisopropyl, 95%, b.p. 110-12°, 1.4393, 0.816, MeCO; *N,N*-di-*i*-butyl, 90%, b.p. 115-18°, 1.4475, 0.828 (Me-Pr ketone); *N,N*-bis(2,6-dimethyl-4-heptyl), 25%, b.p. 183-4°, 1.4554, 0.816, di-*n*-Bu ketone; *N,N*-dimethyl, 79%, b.p. 67-8°, 1.4421, 0.831, HCHO; *N*-monoisopropyl, 63%, b.p. 87°, 1.4465, 0.830, MeCO; *N*-mono-Bu (III), 65%, b.p. 101-2°, 1.4550, 0.833 (butyraldehyde). The first 5 and II had been previously prepd. (cf. Standinger, *et al.*, C.A. 37, 5907 and Graf, 37, 5985). The last 2 were prepd. in aq. solns. which reduces the probability of alkylation of the 2nd amino group.

fm

State Inst. Applied Chem.

*Lebedevskiy, A.I.*  
VIENTENGOLOTS, V.S.; KLEBANSKIY, A.L.

Synthesis of silicon organic compounds. Part 2. Relative activity  
of the different types of contact mass used for the synthesis of  
methylchlorosilanes. Zhur. ob. khim. 27 no.9:2475-2479 8 '57.  
(MIRA 11:3)

(Silane) (Chemistry, Organic--Synthesis)

KLEBANSKIY, A.L.; PIKHTENKOOL'TS, V.S.

Synthesis of silicon organic compounds. Part 3: Study of direct  
synthesis of methylchlorosilanes. Zhur.ob.khim. 27 no.10:2648-2653  
(MIRA 11:4)  
O '57. (Silane)

KLEBANSKIY, A. L.

AUTHORS:

Klebanskiy, A. L. , Grachev, I. V. (Deceased), 75-11-14/56 Kuznetsova, O. K.

TITLE:

The Investigation of the Process of Formation of Diacetylene Compounds From Acetylene Derivatives With One Substituent. I. On the Mechanism of Formation of the Diacetylene Compounds (Issledovaniya reaktsii obrazovaniya diatsetilenovykh soyedineniy iz odnozameshchennykh proizvodnykh atsetilena) (I. O mekhanizme obrazovaniya diatsetilenovykh soyedineniy)

PERIODICAL:

Zhurnal Obshchey Khimii, 1957, Vol. 27, Nr 11. pp.2977-2983 (USSR)

ABSTRACT:

The compounds of the diacetylene series were initially produced with various oxidizing agents by oxidation of the copper - sodium and magnesium bromoderivatives of the acetylenes provided with one substituent. In the present work the attempt is made to carry out, i.e. to improve, the reaction for the formation of diacetylene compounds from acetylene derivatives, with one radical, in the presence of copper salts, as it was already earlier suggested by Zal'kind. As fundamental object of investigation the authors selected the process of the conversion of dimethylacetylenylcarbinol to 2,7-dimethyloctadiene-3,5-diol-2,7. Beside the formation of other diacetylene compounds was also studied, for the purpose of determining the influence of the structure of acetylene compounds

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79-11-14/56

The Investigation of the Process of Formation of Diacetylene Compounds from Acetylene Derivatives With One Substituent. I. On the Mechanism of Formation of the Diacetylene Compounds

upon the process, as well as for the purpose of determining the reaction mechanism. Thus the already suggested mechanism of formation of the diacetylene compounds from acetylene derivatives provided with one substituent in their reactions with copper salts is further developed. It is shown that the formation of the diacetylene compounds in aqueous solutions takes place according to the ionic-radical mechanism, where the ions of the acetylenide form first, facilitated by the copper ions. Further the acetylenide ions are by the ions of the bivalent copper oxidized into radicals which are recombined into the molecule of the diacetylene compound. There are 3 figures, 4 tables, and 13 references, 8 of which are Slavic.

ASSOCIATION: State Institute of Applied Chemistry (Gosudarstvennyy institut prikladnoy khimii)

SUBMITTED: September 27, 1956

AVAILABLE: Library of Congress

1. Diacetylene compounds-Production 2. Diacetylene compounds-Chemical reactions

Card 2/2

KLEBANSKIY, A. L.

79-11-15/56

AUTHORS:

Fikhtengol'ts, V. S. , Klebanskiy, A. L. , Rzhendzinskaya, K. A.

TITLE:

Investigations in the Field of the Synthesis of Organosilicon Compounds. IV. Hydrolysis of Dimethyldichlorosilane With Methylalcohol, Where Noncyclic Polysiloxens and Methylchloride Form (Issledovaniye v oblasti sinteza kremniyorganicheskikh soedineniy. IV. Gidroliz dimetildikhlorosilana metilovym spirtom s obrazovaniyem lineynykh polisiloksanov i khloristogo metila)

PERIODICAL:

Zhurnal Obshchey Khimii, 1957, Vol. 27, Nr 11, pp.2984-2989 (USSR)

ABSTRACT:

Dialkoxo-derivatives are obtained on action of alcohols upon dimethyldichlorosilane  $((CH_3)_2SiCl_2 + 2ROH \rightarrow (CH_3)_2Si(OR)_2 + 2HCl)$ , but their yield is small, the residue being converted to high-molecular compounds. In the presence of aluminum, which binds hydrogen chloride the percentage rate increases up to 80 %, the high-molecular compounds being further reduced. It can be assumed that the high-molecular residue forms in the process of synthesis in the hydrolysis of the ethoxy derivatives with water that separate upon action of hydrogen chloride upon the alcohol. This made the authors think that a stepwise hydrolysis of the dimethyldichlorosilane with formation of noncyclic polysiloxens is possible in the interaction of alcohol and hydrogen chloride. When methyl-

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79-11-15/56

Investigations in the Field of the Synthesis of Organosilicon Compounds. IV. Hydrolysis of Dimethyldichlorosilane With Methylalcohol, Where Noncyclic Polysiloxens and Methylchloride Form

alcohol was used it could be reckoned with the formation of methyl chloride and the regeneration of the initial product which was spent in the synthesis of dimethyldichlorosilane. When catalysts are used ( $H_2SO_4$  and  $FeCl_3$ ) the polysiloxens obtained as final products of the hydrolysis are converted to polycondensation products resembling caoutchouc. - Thus a method was worked out for obtaining noncyclic polysiloxens immediately from dimethylchlorosilane by hydrolysis with methyl alcohol. With an excess of methyl alcohol (250 - 300 %) the methyl chloride used for the synthesis of the dimethyldichlorosilane to be hydrolyzed can be completely regenerated. This method can be employed for the production of resins, tars and stable oils, with utilization of the by-products of the dimethyldichlorosilane synthesis. The rubber-like polycondensation products gave satisfactory practical results after vulcanization. There are 1 figure, 4 tables, and 5 references, 1 of which is Slavic.

SUBMITTED:

October 22, 1956

AVAILABLE:

Library of Congress

Card 2/2

1. Silicon compounds (Organic)-Synthesis
2. Dimethyldichlorosilane-Hydrolysis
3. Methanol-Chemical reactions

AUTHORS: Klebanskiy, A. L., Fikhtengol'ts, V. S., Kariin, A. V. 79-12-28/43

TITLE: Investigations in the Field of the Synthesis of Silicon-Organic Compounds (Issledovaniye v oblasti sinteza kremniyorganicheskikh soyedineniy).  
V. The Synthesis of Polysiloxanes With Combined Radicals (V. Polucheniye polisiloksanov so smeshannymi radikalami).

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, Nr 12, pp. 3321-3324 (USSR).

ABSTRACT: In the present work the authors try to explain the effect of polar substituents on the characteristics of polysiloxanes. For this purpose chloromethyl- and dichloromethyl derivatives of methylsiloxanes were produced by direct chlorination of the corresponding methylchlorosilanes with ultraviolet radiation with subsequent hydrolysis and polycondensation. The chlorination of dimethyldichlorosilane was carried out according to data from publications by conducting the sulfuric-acid dried chlorine through dimethyldichlorosilane in the stirring flask with ultraviolet radiation (quartz lamp with in the flask). After the direct chlorination of diethyl- and trimethylchlorosilane under these conditions the chlorinated final products were isolated. These, as well as their compounds with dimethyldichlorosilane after the hydrolyses with methylalcohol resulted in the corresponding polysiloxanes.

Card 1/2

Investigations in the Field of the Synthesis of Silicon-Organic Compounds. 79-12-28/43

V. The Synthesis of Polysiloxanes With Combined Radicals.

nes. The authors stated the better solubility of the hydrolysis products, which have chloromethyl derivatives, in water and methanol as well as their more complicated polycondensation compared with pure dimethylsiloxanes. The authors also showed that the presence of chloromethyl groups in the caoutchouc-type polysiloxanes causes a certain deterioration of the physico-mechanical parameters of rubber but makes it more resistible against frost. The authors assume that the chlorine atom could be replaced by the SH-group. There are 1 table, and 6 references, 1 of which is Slavic.

SUBMITTED: October 22, 1956.

AVAILABLE: Library of Congress.

1. Silicon compounds (organic) - Synthesis

Card 2/2

*KLEBANSKIY, A. L.*

20-2-25/60  
AUTHORS: Klebanskiy, A. L. , Dolgopol'skiy, I. M. , Dobler, Z. F.  
TITLE: The Role of Complex Compounds and Cations of Complex-Forming  
Components in the Polymerization of Acetylene (Rol' kompleks-  
nykh soyedineniy i kationov kompleksobrazuyushchikh kom-  
ponentov v reaktsii polimerizatsii atsetilena)  
PERIODICAL: Doklady Akademii Nauk SSSR, 1957, Vol. 114, Nr 2, pp.323-326  
(USSR)  
ABSTRACT: It is not possible to consider the mechanism of reaction of  
acetylene polymerization as definitely determined. Study of  
the formation of complex compounds of the acetylene hydro-  
carbons with solutions of CuCl-MCl and of the part of the  
different components of the solution in the polymerization  
made it possible to determine the significance of the dif-  
ferent complex compounds in catalytic reactions, and to con-  
firm the ionic mechanism of the polymerization reaction. In  
connection with the mobility of the  $\pi$ -electrons the ace-  
tylene compounds can be easily polarized by the central cop-  
per atom. During this process, they push the chlorine atoms

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20-2-25/60

The Role of Complex Compounds and Cations of Complex-Forming Components  
in the Polymerization of Acetylene

from the sphere of coordination of copper and take their place. The formation of complex compounds is confirmed by the substantial increase in the solubility of acetylene and of vinylacetylene, together with higher solubility of the  $\text{CuCl}$ , and furthermore by the subsequent crystalline precipitation from the solution, this precipitation containing the complexly bound hydrocarbons. The composition of the precipitation showed that it changes in accordance with the nature of the  $\text{MCl}$ -cation, furthermore also in accordance with the quality of the acetylenehydrocarbons, and in dependence on the ratio  $\text{CuCl} : \text{MCl}$  in the solution. The authors of the paper under review obtained the complex compounds in their individual state and confirm their composition as given by Zürich and Ginsburg. Furthermore, the authors isolated complex compounds of the acetylene and of its tetramers, as well as of divinylacetylene. Their empiric formulae are given. If acetylene or vinylacetylene is solved in  $\text{CuCl}$ - $\text{MCl}$  solutions, then the concentration of the hydrogen atoms increases; at polymerization of vinylacetylene, on the other hand, it decreases. But in the latter case further complex compounds are formed which

Card 2/4

20-2-25/60

The Role of Complex Compounds and Cations of Complex-Forming Components  
in the Polymerization of Acetylene

contain  $\text{HCl}$ . A close relationship between the ionizing capacity of the complex compounds and the catalytic activity of their solutions was discovered. The latter increases when the hydrogen ionization in the hydrocarbon is increased. Water is necessary for the ionic hydration of the complex compounds. Without water, no ionization takes place, and consequently also no acetylene polymerization. The above confirms the ionic mechanism of acetylene polymerization. The dependence of the degree of ionization of the acetylene complex compounds is reproduced on Figure 3 contained in the paper under review. Also amino salts can be used as complex components. The amines are arranged in an increasing series with respect to their degree of polarity, characterized by the constant of dissociation. Figure 4 of the present paper illustrates the dependence of the activity of a catalyzer upon the quality of the amines. The transformation of vinylacetylene into acetylenetetramer increases with decreasing molecular weight of the cation. The activity of the catalyzer

Card 3/4

[KLEBANSKIY, A. L.]

**AUTHORS:** Mal'nova, G. N., Mikheyev, Ye. P.,  
Klebanskiy, A. L., Golubtsov, S. A., and  
Filimonova, N. P.

20-4-21/52

**TITLE:** On the Catalytic Phenylation of Hydrogenous Alkyl-  
Chlorosilanes by Benzene (O kataliticheskom fenilirovani  
vodorododerzhashchikh alkilkhlorosilanov benzolom).

**PERIODICAL:** Doklady AN SSSR, Vol. 117, Nr 4, pp. 623-625 (USSR) 1957

**ABSTRACT:** This reaction of the alkylchlorosilanes mentioned in the title above with aromatic hydrocarbons has been treated only insufficiently in scientific literature. A short literary review reveals among other facts that as yet in almost every case elements from the third group of the periodic system have been used as catalyzers. The authors preferred to use boric acid as a catalyzer sufficiently active and fitting for their purpose. If it is added to the reaction mixture in a quantity of 0,1% the formation of phenyl-trichlorosilane is restrained almost completely. Otherwise there is hardly any possibility of separating it from methyl-phenyl-dichlorosilane by rectification. The increase of compression in the autoclave - chiefly caused by

Card 1/3



On the Catalytic Phenylation of Hydrogenous Alkyl-  
Chlorosilanes by Benzene

20-4-21/52

elimination of hydrogen ceases, according to the temperature of synthesis, at 290° after one hour, at 250° after two hours. Warming for a longer time is not profitable (see patents, references 2-4,6) as in that case the exploit of the final product decreases. With 0.1% boric acid the optimal temperature is by 240°. If the temperature is caused to fall by 5-10° the reaction is decisively retarded. The comparatively small exploit of alkyl-phenyl-dichlorosilane is caused on the whole by the high capability of reaching of the alkyl-dichlorosilanes which suffer not only phenylation but different other transformations such as changes of thermal rearrangement, condensation, and reaction with alkyl-phenyl-dichlorosilane. The details of table 2 confirm the assumption that the augmentation of the proportion of benzene will increase the exploit of alkyl-phenyl-dichlorosilane. Under optimal conditions it reaches 40% of the reacting methyl-dichlorosilane. Finally by-products are mentioned. The reciprocal reaction of benzene and ethyl-dichlorosilane in presence of boric acid is analogous. The optimal temperature is about 250°.

Card 2/3

KLEBAN'SKIY, A.L.; PONOMAREV, A.I.; KUDINA, V.I.

Preparation of carboxymethylheptamethylcyclotetrasiloxane. Khim.  
nauka i prom. 3 no.2:285-286 '58. (MIRA 11:6)

1. Nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im.  
S.V. Lebedeva..

(Siloxanes)

**AUTHORS:** Klebanskiy, A. L., Sayadyan, A. G., 79 28 3-1/61  
Barkhudaryan, M. G.

**TITLE:** Investigation of the Polycondensation Mechanism of 1,3-Dichlorobutene-2 Under Action of Friedel - Crafts - Gustavson Catalysts I (Izucheniye mekhanizma polikondensatsii 1,3-dikhlorbutena-2 pod vliyaniyem katalizatorov Fridelya-Kraftsa-Gustavsona I)

**PERIODICAL:** Zhurnal Obshchey Khimii. 1958, Vol. 28, Nr 3, pp. 569-574 (USSR)

**ABSTRACT:** The polycondensation of 1,3-dichlorobutene-2 under action of Friedel - Crafts - Gustavson catalysts was announced by the authors already earlier (ref.1). Other references are lacking. The polymers of these compounds are, however, of interest as they are film-forming substances. Besides, this polycondensation models to a high degree the vulcanization process of polychloroprene ( $\text{CH}_2=\text{CH}-\text{CCl}=\text{CH}_2$ ) under the action of metal oxides. The polycondensation of 1,3-dichlorobutene-2 was carried out by the authors in the presence of  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$  and  $\text{SnCl}_4$ . In all cases low-molecular and resinous products are observed. the polycondensation

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Investigation of the Polycondensation Mechanism of 1,3-  
-Dichlorobutene-2 Under Action of Friedel-Krafts-Gustavson  
Catalysts I

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process taking place most clearly mainly under the formation of high-molecular polymers when  $\text{AlCl}_3$  is used. The reaction with  $\text{FeCl}_3$  takes place slowly, which makes it possible to isolate the primary low-molecular polymers. Dimers as well as low-molecular polymers were separated. In investigating the composition and structure of low-molecular compounds the dimer  $\text{C}_8\text{H}_{12}\text{Cl}_4$  and the product  $\text{C}_8\text{H}_{11}\text{Cl}_3$  were found. The

increased mobility of the chlorine atom increases the capability of forming the complex  $\text{CH}_3\text{-CCl}=\text{CH-CH}_2^+ \cdot \text{FeCl}_4^-$

under the influence of the said catalysts.- This complex is bound to dichlorobutene according to scheme 1. The obtained dimer 2,6,6-trichloro-5-chloromethylheptene-2 has the structure (II) which was supported by ozonization, as in the products of decomposition of acetic acid (80% of the theoretical yield)  $\beta$ -chloromethyl- $\gamma$ -dichlorovalerianic acid (62,9%) and hydrochloric acid (91%) were found. The formation of the above mentioned  $\text{C}_8\text{H}_{11}\text{Cl}_3$  side product is

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tentatively explained by scheme 2. In the reaction process

Investigation of the Polycondensation Mechanism of 1,3-  
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therefore a binding of two molecules 1,3-dichlorobutene-2 exists under the formation of 2,6,6-trichloro-5chloromethylheptene-2; from this hydrogen chloride is split off under the formation of 2,6-dichloro-5-chloromethylheptadiene-2,5. At the same time polymers of high molecular weight are formed the composition of which confirms the proposed polycondensation scheme. A vulcanization process of polychloroprene with metal oxides by condensation was suggested, which takes place under the action of the metal chlorides forming in it. There are 5 references, 4 of which are Soviet.

SUBMITTED: March 5, 1957

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79-28-3-2/61

AUTHORS: Klebanskiy, A. L., Sayadyan, A. G., Barkhudaryan, M. G.

TITLE: The Reaction of 1,3-Dichlorobutene-2 With Chloroprene Under the Action of Friedel - Crafts - Gustavson Catalysts. II (Vzaimodeystviye 1,3-dikhlorbutena-2 s khloroprenom pod vliyaniyem katalizatorov Fridelya - Kraftsa - Gustavsona. II)

PERIODICAL: Zhurnal Obshchey Khimii. 1958, Vol. 28, Nr 3, pp. 574-578 (USSR)

ABSTRACT: In connection with the investigations carried out by one of the authors on the synthesis of compounds modelling the basic structural types of synthetic rubber with regard to their different reactivity, also the reaction of crotyl chlorides of different structure with chloroprene, isoprene and divinyl were investigated. Here the results of the reaction of 1,3-dichlorobutene-2 with chloroprene in the presence of the catalysts  $AlCl_3$  and  $FeCl_3$  are given. In both cases low-molecular and resinous products were observed. When using  $AlCl_3$ , the yield of the binding product (1 mol. to 1 mol.) was very small. With an increase of the concentration of the catalyst

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Action of Friedel - Crafts - Gustavson Catalysts. II

mainly the formation of high-molecular compounds is taking place which makes more difficult the isolation of low-molecular compounds. The ratio between the initial products exercised great influence on the final products, the yield of the primary binding product increasing with the increase of the excess of 1,2-dichlorobutene-2. As results of the reaction of 1,3-dichlorobutene-2 with chloroprene as primary product the formation of six compounds can be expected (see formulae (I), (II), (III), (IV), (V), (VI)). Their structure was proved by ozonization, as in the products of decomposition acetic acid, chloroacetic acid and succinic acid (75,6% - 80,3% and 81,09%) were found. It must be assumed that in this reaction the step-by-step condensation takes place as follows: First the compound  $\text{CH}_3\text{CCl}=\text{CHCH}_2\text{CH}_2\text{CCl}=\text{CHCH}_2\text{Cl}$ , then  $\text{CH}_3\text{CCl}=\text{CHCH}_2(\text{CH}_2\text{CCl}=\text{CHCH}_2)_2\text{Cl}$ , then  $\text{CH}_3\text{CCl}=\text{CHCH}_2(\text{CHCCl}=\text{CHCH}_2)_3\text{Cl}$ , etc. Such reactions are described in publications as "telomerization". Thus it was shown that in the presence of the two catalysts 1,3-dichlorobutene-2 combines with chloroprene in the position

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The Reaction of 1,3-Dichlorobutene-2 With Chloroprene Under 79-28-3-2/61  
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1,4, forming products containing one, two, three or more molecules. The product of the reaction of one molecule 1,3-dichlorobutene-2 with one molecule chloroprene has the structure of 1,3,7-trichloro-octadiene-2,6. There are 8 references, 3 of which are Soviet.

SUBMITTED: March 5, 1957

Card 3/3



AUTHORS: Klebanakiy, A. L., Sayadyan, A. G., 79-28-4-7/60  
Barkhudaryan, M. G.

TITLE: Interaction of the 1,3-Dichlorobutene-2 With Isoprene  
 and Divinyl Under the Action of  $\text{FeCl}_3$ . III (Vzaimodeyst-  
 viye 1,3-dikhlorbutena-2 s izoprenom i divinilom pod  
 vliyaniyem  $\text{FeCl}_3$ . III)

PERIODICAL: Zhurnal Obshchey Khimii, 1958. Vol. 28, Nr 4,  
 pp. 881-884 (USSR)

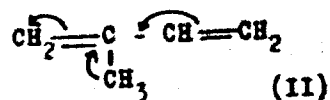
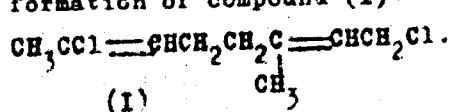
ABSTRACT: In the previous paper the investigation results of the  
 reaction of 1,3-dichlorobutene-2 with chloroprene under  
 the action of the catalysts by Fridel' - Crafts - Gustav-  
 son (Zhurnal Obshchey Khimii, 1958, Vol. 28, pp. 574)  
 were demonstrated. The authors continued work in this  
 direction and investigated the reaction of the interac-  
 tion of 1,3-dichlorobutene-2 with isoprene and divinyl  
 in the presence of  $\text{FeCl}_3$ . In both cases the formation  
 of low molecular as well as of resinoid products was  
 observed. They did not succeed in precipitating the

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Isoprene and Divinyl Under the Action of  $\text{FeCl}_3$  - III

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primary product by using the catalyst  $\text{AlCl}_3$ . For this reason further experiments were carried out only with the catalyst  $\text{FeCl}_3$ . On this occasion concentration did not surpass 0.25 mol %. In the case of higher concentration the number of the high molecular products increased with simultaneous decrease of the yield of the primary addition compound, which rendered difficult the precipitation of the latter. In reactions with isoprene as well as in those with divinyl the compound of the products influences the interaction of the initial substances on which occasion the yield of the primary additional compound increases with the increase of 1,3-dichlorobutene-2 excess. In the addition of 1,3-dichlorobutene-2 as primary product to isoprene the formation of 6 products may be expected as result according to the direction of the addition: 1,4; 4,1; 1,2; 2,1; 3,4 and 4,3. It was found that the addition mainly takes place in position 1,4 with the formation of compound (I).

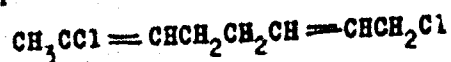


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Interaction of the 1,3-Dichlorobutene-2 With  
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The structure of the formed product was proved by ozonization. No addition products of two 1,3-dichlorobutene-2 molecules to one isoprene molecule are observed in the reaction mixture. In the addition of 1,3-dichlorobutene-2 as primary product to divinyl the formation of three different reaction products can be expected according to the direction of the addition (1,4; 1,2 or 2,1). The method of ozonolysis was used for the determination of the structure. The result shows that the addition takes place also in this case mainly in the 1,4 position and that a compound:



forms.

Also in this case no addition products of two 1,3-dichlorobutene-2 molecules to one divinyl molecule were observed in the reaction mixture. The results of the investigation proved that in the case of chloroprene as well as with isoprene the reaction of telomerization takes place

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Interaction of the 1,3-Dichlorobutene-2 With  
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under the formation of higher molecular compounds.  
Conclusion: It was found that in the interaction of  
1,3-dichlorobutene-2 with isoprene and divinyl tarry high  
molecular material as well as low molecular primary  
addition products are formed. 1,7-dichloro-3-methyl  
octadiene-2,6- an addition product of 1,3-dichlorobutene-2  
to isoprene in position 1,4 was precipitated. 1,7-dichloro  
octadiene-2,6- an addition product of 1,3-dichlorobutene-2  
to divinyl in position 1,4 was precipitated.  
There is 1 table. 0 references.

SUBMITTED: March 25, 1957

Card 4/4

KIRBANSKIY, A.L.; VILISOVA, M.S.

Synthesis and polycondensation of N-alkyl derivatives of hexamethylenediamine. Part 1: Synthesis of N,N'-dialkyl derivatives of hexamethylenediamine. Zhur. ob. khim. 28 no. 4:1066-1072 Ap '58.  
(Hexanediamine) (Alkylation) (MIRA 11:5)

79-20-4-49/60

**AUTHORS:** Klebanakiy, A. L. , Vilesova, M. S.

**TITLE:** Research in the Field of the Synthesis and Polycondensation of N-Alkyl Derivatives of Hexamethylene Diamine (Issledovaniye v oblasti sinteza i polikondensatsii N-alkilproizvodnykh geksametilendiamina) II. On the Synthesis of N-Monoalkyl Derivatives of Hexamethylene Diamine (II. O sinteze N-mono-alkilproizvodnykh geksametilendiamina)

**PERIODICAL:** Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 4, pp. 1073-1075 (USSR)

**ABSTRACT:** The production of N-monosubstituted hexamethylene diamines by means of the normal method of reducing alkylation (Ref 1) is connected with great difficulties. The carbonyl compound may, at least in the initial stage of the reaction, react with the amino group of the free as well as with the amino group of the already monosubstituted diamine. Thus, a compound of N-mono- and N,N'-dialkyl diamines which can be separated only with difficulties and which contains a considerably part of the disubstituted components forms. In order to conduct reaction to the side of the N-monosubstitution the observation made by the authors was used that

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Derivatives of Hexamethylene Diamine. II. On the Synthesis of N-Mono-  
alkyl Derivatives of Hexamethylene Diamine

solid hydrates insoluble in water may form from N-mono- as well as from N,N'-dialkylated diamines. For this reason the reaction is carried out best in the aqueous medium and the ratio between the quantity of the alkylating compound, and hexamethylene diamine was selected correspondingly lower (up to 1 mol per 1 mol diamine). Greater yield of N-mono-substituted diamine is achieved by the fact that it precipitates from the aqueous solution in the form of the solid hydrate. Due to this reason the probability of the reaction of the second amino group with the alkylating agent is reduced and the reaction is shifted mainly to the side of N-monoalkylation. The formation of hydrates was investigated quantitatively by the example of the disubstituted derivatives, especially by the example of N,N'-di-n-butyl and N,N'-diisopropyl hexamethylene diamine. Disubstituted diamines form crystallized white hydrates if water is added, and also in an atmosphere saturated with steam, and in air. In drying with  $P_2O_5$  in the exsiccator water is completely separated and the re-formed diamine proves identical with

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Research in the Field of the Synthesis and Polycondensation of N-Alkyl  
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the original diamine. It could be observed experimentally that 1 mol of the disubstituted diamine rapidly absorbs 2 mols of water and then forms a hydrate; further absorption of water takes place much more slowly. At the given conditions 1 mol diamine absorbed maximally 4 mols water. The dehydrate of the N,N'-di-n-butyl-hexamethylene diamine is insoluble in water, the dihydrate of N,N'-diisopropyl-hexamethylene diamine dissolves in the excess water. Also N,N'-diisobutyl-, N,N'-di-n-butyl-2-hexamethylene diamine and others form hydrates. Monosubstituted diamines equally form crystallized hydrates in the air (in an atmosphere saturated with steam). The decrease in the yield of N,N'-dialkyl diamines and the formation of a certain amount of N-monosubstituted diamine at the carrying out of the reaction of the reducing alkylation in water is obviously explained by the formation of these hydrates. The method of representation of mono-substituted derivatives was elaborated by means of the example of N-mono-n-butyl hexa-

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Research in the Field of the Synthesis and Polycondensation of N-Alkyl Derivatives of Hexamethylene Diamine. II. On the Synthesis of N-Mono-alkyl Derivatives of Hexamethylene Diamine

methylenediamine, however, it can also be used for the synthesis of other monosubstituted derivatives which form hydrates insoluble or difficultly soluble in water. The hydrate of N-monoisopropyl-hexamethylenediamine is soluble in excess water. However, also in this case the yield of the N-monosubstituted product is increased in carrying out the reaction in the aqueous medium.

In an experimental part the alkylation by means of the n-aldehydes of the aliphatic series, and by acetone is described in detail. There are 1 figure, 2 tables, and 1 reference, 1 of which is Soviet.

SUBMITTED: April 11, 1957

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**AUTHORS:** Klebanskiy, A. L., Vilesova, M. S. 507/79-28-6-19/63

**TITLE:** Investigation in the Field of the Synthesis and Polycondensation of N-Alkyl Derivatives of the Hexamethylenediamine (Issledovaniye v oblasti sinteza i polikondensatsii N-alkilproizvodnykh geksametilendiamina) III. On the Influence of the Structure of the Substituting Radical on the Direction of Reaction of the Alkylation of Hexamethylenediamine (III. O vliyani stroyeniya zameshchayushchego radikala na napravleniye reaktsii alkilirovaniya geksametilendiamina)

**PERIODICAL:** Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1524-1528 (USSR)

**ABSTRACT:** The earlier investigations (Ref 1) of the reduction alkylation of hexamethylene diamine made it possible to the authors to determine some dependences of the radical structure of the carbonyl compound on the reactivity in the alkylation; among the carbonyl compounds formaldehyde plays a special rôle. Different from reactions carried out earlier with formaldehyde the alkylation had to be carried out in neutral medium and the hydrochloric salt of hexamethylene diamine

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SOV/ 79-28-6-19/63

Investigation in the Field of the Synthesis and Polycondensation of N-Alkyl Derivatives of the Hexamethylenediamine. III. On the Influence of the Structure of the Substituting Radical on the Direction of Reaction of the Alkylation of Hexamethylenediamine

had to be used. At the molar ratio of diamine to aldehyde -1:2 the asymmetric N-dimethylhexamethylene diamine (75 %) of the formula  $(CH_3)_2N-(CH_2)_6-NH_2$  was obtained as main product. The high-boiling fraction obtained as secondary product contained mainly the tri-substituted diamine. It is shown that the chosen direction of the reduction alkylation of hexamethylene diamine in the direction to the N,N'-dialkylation is determined by two opposite influences, viz. by the increase of the reactivity of the substituted amino group and by the steric effect of the substituent. Beginning with isopropyl and higher an exclusive direction of the reaction to the side of the N,N'-disubstitution is observed. On the introduction of the ethyl- and n-propyl radical the synthesis of the pure symmetric hexamethylene derivative is made difficult. On the introduction of the methyl the reaction takes place completely to the side of the formation of the asymmetric product of substitution. The introduction of a tertiary butyl group to the amino group of the hexamethylene diamine is not

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achieved whereas trimethylsilyl easily substitutes both hydrogen atoms under the formation of a four times-substituted compound. There are 2 tables and 3 references, which are Soviet.

SUBMITTED: May 25, 1957

1. Alkyl derivatives--Synthesis    2. Methyl hydrazines--Chemical reactions

Card 3/3

**AUTHORS:** Klebanskiy, A. L., Vilesova, M. S. SOV / 79-28-6-20/63

**TITLE:** Investigation in the Field of the Synthesis of N-Alkylhexamethylene Diamine Derivatives and Their Polycondensations (Issledovaniye v oblasti sinteza N-alkilproizvodnykh geksametilendiamina i ikh polikondensatsii) V. Some Problems Concerning the Reaction Kinetics of the Reduction Alkylation of Hexamethylene Diamine (V. Nekotorye voprosy kinetiki reaktsii vosstanovitel'nogo alkilirovaniya geksametilendiamina)

**PERIODICAL:** Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1528-1534 (USSR)

**ABSTRACT:** The purpose of the present paper was to explain: 1) The dependence of the reaction velocity on the conditions under which the process takes place, and 2) The influence of the structure of the alkylating compound on the reaction velocity of the reduction alkylation of hexamethylene diamine. Based on the results which were obtained by the authors in the synthesis of N-substituted diamines it was possible when using these data to determine the course of reaction and to

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Investigation in the Field of the Synthesis of N-Alkylhexamethylene Diamine  
Derivatives and Their Polycondensations. V. Some Problems Concerning the  
Reaction Kinetics of the Reduction Alkylation of Hexamethylene Diamine

carry out the comparison with various alkylating compounds. The investigation of the reaction of the reduction alkylation of hexamethylene diamine with aldehydes and ketones at increased (100 - 50 atmospheres) as well as at normal atmospheric pressure showed that this reaction apparently is of suction character which is limited by the diffusion stage of the reaction component of solution and catalyst. It was shown that the reaction velocity does not depend on the concentration of the components and their conversion in the reaction process (Figs 1 - 5). On the other hand it also considerably depends on the structure of the alkylating aldehyde or ketone. It was found that the reactions of the reduction alkylation of hexamethylene at normal pressure and above 50 atmospheres absolute pressure are of zero-th order, and within the interval of from 10 to 40 atmospheres they are of first order; this fact can be explained by the incomplete suction saturation of the catalyst within this pressure interval. It was shown that the above mentioned reaction velocity is on the one hand dependent on the relative polari-

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Derivatives and Their Polycondensations. V. Some Problems Concerning the  
Reaction Kinetics of the Reduction Alkylation of Hexamethylene Diamine

ty of the alkylating compounds and on the other hand by the  
steric hindrances caused by the structure. The second fac-  
tor plays a rôle only in the case of ramified carbonyl com-  
pounds. There are 8 figures, 3 tables, and 3 references, 2  
of which are Soviet.

SUBMITTED: May 25, 1957

1. Alkyl derivatives--Synthesis      2. Methyl hydrazines--Chemical  
reactions

Card 3/3

AUTHORS: Kleban'skiy, A. L., Vilenova, M. S. SOV/79-28-7-11/64

TITLE: Investigation in the Field of the Synthesis of the N-Alkyl Derivatives of Hexamethylene Diamine and Their Polycondensations (Issledovaniye v oblasti sinteza N-alkilproizvodnykh geksametilendiamina i ikh polikondensatsii) V. On the Reaction Mechanism of the Reduction Alkylation of Hexamethylene Diamine (V.O mekhanizme reaktsii vosstanovitel'nogo alkilirovaniya geksametilendiamina)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 7, pp. 1767 - 1772 (USSR)

ABSTRACT: The problem of the possible intermediate products and of the role played by the catalyst is of importance for the explanation of the reaction mechanism of the reduction alkylation of hexamethylene diamine. It is generally assumed that in such reactions an azomethine base, i.e. Schiff's base (Ref 1) occurs as intermediate product. In order to determine its presence in the case investigated the reduction velocities of the mixture of hexamethylene diamine butyric acid aldehyde and of the corresponding azomethine base with the formula  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{NH}(\text{CH}_2)_6\text{NH}-\text{CHCH}_2\text{CH}_2\text{CH}_3$  were compared to each

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Investigation in the Field of the Synthesis of the  
N-Alkyl Derivatives of Hexamethylene Diamine and Their Polycondensations.  
V. On the Reaction Mechanism of the Reduction Alkylation of Hexamethylene  
Diamine

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other in alcoholic solution. From figure 1 may be seen that the reduction of the above mentioned mixture takes place considerably more rapidly than that of the pure Schiff's base. The investigations showed that according to the infrared spectra and the polarographic data obtained a Schiff's base is present in the mixture of hexamethylene diamine and butyric acid aldehyde. In the hydration with hydrogen the reduction velocity of Schiff's base is considerably higher at the moment of separation than that of the mixture of hexamethylene diamine and the carbonyl compound. A reaction mechanism of the reduction alkylation is suggested according to which the diamine and the carbonyl compound are individually chemically absorbed, converted and reduced in the absorbed state. The velocity of the reduction alkylation is determined by the chemical absorption of the single reaction component. The reduction of the base existing in the solution does not determine the course of the process as a whole. There are 3 figures, 1 table, and 3 refer-

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Investigation in the Field of the Synthesis of the SOV/79-28-7-11/64  
N-Alkyl Derivatives of Hexamethylene Diamine and Their Polycondensations.  
V. On the Reaction Mechanism of the Reduction Alkylation of Hexamethylene  
Diamine

ences, 3 of which are Soviet.

SUBMITTED: May 25, 1957

1. Methyl amines--Synthesis
2. Methyl amines--Reduction
3. Alkyl derivatives--Synthesis
4. Catalysts--Performance
5. Infrared spectrum--Applications
6. Condensation reactions

Card 3/3

**AUTHORS:**

Klebanskiy, A. L., Vilesova, M. S.

SOV/79-28-7-12/64

**TITLE:**

Investigation in the Field of the Synthesis of N-Alkyl Derivatives of Hexamethylene Diamine and Their Polycondensations (Issledovaniye oblasti sinteza N-alkilproizvodnykh geksametilendiamina i ikh polikondensatsii) VI. The Synthesis of the Polyamines Proceeding From the N-Alkylated Hexamethylene Diamine. The Synthesis of the Partially N-Alkylated Polyamides (VI. Sintez poliaminov na osnove N-alkilirovannogo geksametilendiamina. Polucheniiye chastichno N-alkilirovannykh poliamidov)

**PERIODICAL:**

Zhurnal obshchey khimii, Vol. 28, Nr 7, pp 1772 - 1776 (USSR)

**ABSTRACT:**

In the present investigation the author synthesized products of various substituted diamines (in the positions N<sub>1</sub> and N<sub>2</sub>) and their mixtures with not-substituted diamines in order to disturb the crystalline structure of the polyamide and to furnish it with elastic properties. The N,N'-disubstituted diamines which by polycondensation lead to polyamides without hydrogen bindings between the chains were then treated with diisocyanate. Thus two types of polyamides were obtained which were principally different from each other. The first type is formed by polycondensation

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Investigation in the Field of the Synthesis of N- Alkyl Derivatives of Hexamethylene Diamine and Their Polycondensations. VI. The Synthesis of the Polyamines Proceeding From the N-Alkylated Hexamethylene Diamine. The Synthesis of the Partially N-Alkylated Polyamides

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and consists of comparatively short polymer molecules combined by hydrogen. The properties of these products are not only determined by the number of the existing hydrogen bindings but also by the structure of the substituted radical. The polymers of the second type do not have such a binding. Their basic polyamide chains are lengthened and cause valence bridge bonds between the chains to be formed with diisocyanate at the expense of the reaction of their end groups, which are produced in the reaction of the diisocyanate with the forming carbamide groups. These polymers (of second type) are of importance for the modification of their physicochemical properties. Polyamides of various degree and of different order with respect to their N-substitution, based on the conversion of the N,N'-di- and N-monoisopropyl hexamethylene diamine with adipic acid were obtained and characterized. There are 2 figures, 3 tables, and 7 references, 3 of which are Soviet.

SUBMITTED:  
Card 2/3

May 31, 1957

AUTHORS:

Klebanskiy, A. L., Vilesova, M. S.

SOV/79-28-7-13/64

TITLE:

Investigation in the Field of the Synthesis of the N-Alkyl Derivatives of Hexamethylene Diamine, and Their Polycondensations (Issledovaniye v oblasti sinteza N-alkilproizvodnykh geksametilendiamina i ikh polikondensatsii) VII. The Complete Production of N-Alkylated Polyamides and the Coupling of Their Chains With Diisocyanate (VII. Polucheniye polnost'yu N-alkilirovannykh poliamidov i sochetaniye ikh tsepey diizotsianatom)

Periodical:

Zhurnal obshchey khimii, 1958, Vol. 28, Nr 7, pp. 1777 - 1781 (USSR)

ABSTRACT:

Diisocyanate was by many scientists (Ref 1) used as means for the lengthening of the polyester chains. This method is employed in the synthesis of N-substituted polyamides for the first time; it consists of two stages: 1) A complete synthesis of the N-substituted polyamides proceeding from adipic acid and N,N'-dialkyl hexamethylene diamine with various substituents. 2) The lengthening of the chains of the obtained polyamide, and transformation of the linear polymer into a space polymer by a reaction with diisocyanate according to the mentioned scheme.

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Investigation in the Field of the Synthesis of the N- Alkyl Derivatives of Hexamethylene Diamine, and Their Polycondensations. VII. The Complete Production of N-Alkylated Polyamides and the Coupling of Their Chains With Diisocyanate SOV/79-28-7-13/64

In order to secure the chain formation of the polyamide in the lengthening by means of diisocyanate a polymer with secondary amino groups at the chain terminals had to be obtained, which was achieved by excess diamine. Therefore no salts served as initial products but a free substituted diamine and adipinic acid. Concluding N-alkylated polyamides were synthesized with different substituents and it was shown that polyamides with ramified radicals (isopropyl-, butyl-2-) of wax-like character as well as those with line radicals (n-propyl-, n-butyl-) of balsam-like character are soluble in benzene. It was found that in the conversion of the N-alkylated polyamides with diisocyanate a lengthening of the chains take place on which occasion polymers with ramified substituents form solid, and even brittle products, whereas such with linear substituents form elastic products. The second treatment with excess diisocyanate leads to polyamides of space structure. There are 1 figure, 4 tables, and 3 references, 2 of which are Soviet.

Card 2/3

Investigation in the Field of the Synthesis of the N- SOV/79-28-7-13/64  
Alkyl Derivatives of Hexamethylene Diamine, and Their Polycondensations. VII.  
The Complete Production of N-Alkylated Polyanides and the Coupling of Their  
Chains With Diisocyanate

SUBMITTED: May 31, 1957

1. Alkyl derivatives--Synthesis 2. Amides--Production 3. Amides  
--Molecular structure 4. Diisocyanates--Molecular structure

Card 3/3

**AUTHORS:** Klebenskiy, A. L., Krasinskaya, D. M. 507/75-28-8-13/66

**TITLE:** Synthesis of the Alkoxy Derivatives of Divinyl Acetylene  
(Sintez alkoksiproizvodnykh divinilatsetilena)  
VII. Concerning the Orientation of the Addition of Ethyl Alcohol to Divinylacetylene (VII. O napravlenii prisoedineniya etilovogo spirta k divinilatsetilenu)

**ISSN:** Zhurnal obshchey khimii, 1958, Vol. 28, Nr 8, pp.2061-2064 (Rus.)

**ABSTRACT:** In a previous report (Ref 1) it was shown that the addition of various alcohols to divinylacetylene, in the presence of a sodium alkoxy compound and at the boiling point of the mixture, takes place at varying positions. One could assume that the locus of addition was dependent upon the reaction temperature or the structure of the radical. In order to clarify the influence of the reaction temperature on the position at which ethyl alcohol adds to divinyl acetylene a decomposition reaction was carried out in the presence of a sodium alkoxy compound and at a lowered temperature of 60° (previous temperature: 85 - 95°), a temperature corresponding to the reaction temperature for methyl alcohol. It was found that the addition takes place primarily in the 1 and 4 positions,

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Synthesis of the Alkoxy Derivatives of Divinyl  
Acetylene. VII. Concerning the Orientation of the Addition of Ethyl Alcohol  
to Divinylacetylene

307/79-28-8-13/66

as is the case with methyl alcohol, and not in the 1 and 6 positions as it had at the higher temperature. The rate of addition of the ethyl alcohol is clearly less than that for methyl alcohol at the same temperature. The yield of ethoxy derivative after 300 hours was 14 %, while the methoxy yield was 12 - 13 % after 40 - 60 hours, both calculations based on the starting carbonic acid. The addition product of the ethyl alcohol is 3-ethoxyhexatriene-1,3,4 (Formula I). Its structure was proved by ozonolysis, whereby formic, acetic, and oxalic acids were obtained. Thus it was shown that the addition of ethyl alcohol to divinylacetylene is conditioned by the reaction temperature (see Formula I and Formula II). Further investigations showed that an isomerization results when the mixture is heated for a longer time, and that the primary addition loci are the 1 and 4 positions, the 1 and 6 position forms then resulting from subsequent isomerization. There are 3 references, 2 of which are Soviet.

SUBMITTED:  
Card 2/3

June 27, 1957

NOV/79-28-3-11/66  
Synthesis of the Alkoxy Derivatives of Divinyl Acetylene. VII. Concerning  
the Orientation of the Addition of Ethyl Alcohol to Divinylacetylene

Card 3/3

AUTHORS: Klebanskiy, A. L., Sayadyan, A. G., SOV/79-28-12-20/41  
Barkhudaryan, A. G.

TITLE: Telomerization of Chloroprene in the Reaction With 1,3-Dichloro-Butene-2 Under the Action of  $FeCl_3$ . IV (Telomerizatsiya khloroprena pri vzaimodeystvii s 1,3-dikhlorbutenom-2 pod vliyaniyem  $FeCl_3$ . IV)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol 28, Nr 12, pp 3253 - 3258 (USSR)

ABSTRACT: According to references 1 and 2 the activity of chloroprene in telomerization reactions under the action of ion catalysts is lower than in other diolefins. This property contradicts the comparatively higher reactivity of chloroprene in the radical polymerization, the velocity of which is higher by 760 times than that of isoprene if the process is carried out in a homogeneous mass. To determine the effect of the ratio between 1,3-dichloro-butene-2 (I) and chloroprene (II) in the presence of  $FeCl_3$  upon the molecular weight of the forming telomers the authors carried out the telomerization within the wide range of the molar ratio (I) : (II) of from 2:1 to 1:500, which is

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Telomerization of Chloroprene in the Reaction With  
1,3-Dichloro-Butene-2 Under the Action of  $\text{FeCl}_3$ . IV

SOV/79-28-12-20/41

of theoretical and practical interest. In the chloroprene rectification product and especially in the raw product there are impurities of dichloride and  $\text{FeCl}_3$  contained which cause the formation of low-molecular polymers in the rectification, and even on longer standing. These impurities coming from the material of the apparatus used change the molecular weight and plasticity of the polymers forming from chloroprene. In the emulsion polymerization these impurities do not exert any influence as the iron chloride is hydrolyzed and becomes inactive (see results on all this given in table 1 and in figures 1-4). By investigation of the polymers obtained the authors proved that 1,3-dichloro-butene-2 is a component of all polymers. Its quantities decrease with decrease of its molecular ratio to chloroprene; the medium molecular weight of the polymers increases accordingly. A sufficiently good congruence of the molecular weights was found, which were determined cryoscopically and viscosimetrically according to the chlorine to be saponified. This is proof of the telomerization scheme suggested on the action of  $\text{FeCl}_3$ .

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Telomerization of Chloroprene in the Reaction With  
1,3-Dichloro-Butene-2 Under the Action of  $\text{FeCl}_3$ . IV

SOV/79-28-12-20/41

There are 4 figures, 2 tables, and 2 references, 1 of  
which is Soviet.

ASSOCIATION: Yerevanskiy politekhnicheskiy institut im. Karla Marksa  
(Yerevan Polytechnic Institute imeni Karl Marks)

SUBMITTED: October 14, 1957

Card 3/3

DOLGOPOL'SKIY, I.M.; KIMBANSKIY, A.L.; KRASINSKAYA, D.M.

Polymerisation of divinylacetylene. Zhur. prikl. khim. 31 no.9:  
1403-1408 B '58. (MIRA 11:10)  
(Acetylene) (Polymerisation)

KLEBANSKIY, A.L.; GRACHEV, I.V.; KUZNETSOVA, O.M.

Oxidation of dimethylacetylenylcarbinol by copper chlorides in an ammonia solution. Zhur.prikl.khim. 31 no.12:1869-1875 D '58.  
(MIRA 12:2)

(Propynol) (Oxidation) (Copper chlorides)

5(3)

AUTHORS:

Kal'nova, G. M., Mikheyev, Ye. P.,  
Klebanakiy, A. L., Filimonova, N. P.

SOV/20-123-4-33/53

TITLE:

Catalytic Interaction Between Alkyl Dichloro Silanes and  
Halogen Substitution Products of Benzene (Kataliticheskoye  
vzaimodeystviye alkildikhlorosilanov s galoizameshchennymi  
benzola)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 4,  
pp 693 - 695 (USSR)

ABSTRACT:

The above interaction is mentioned in only a few patents  
(Ref 1). The authors investigated the same interaction of  
methyl dichloro silane with chloro benzene and fluoro benzene  
as well as the same reaction of ethyl dichloro silane with  
chloro benzene. Boric acid with its numerous advantages was  
used as catalyst, or more accurately as source material for  
the catalyst. A) Reaction of methyl and ethyl dichloro silane  
with chloro benzene. The temperature necessary for introducing  
the reaction amounts to 255° (methyl dichloro silane); it is  
10° higher for ethyl dichloro silane. Table 1 shows the

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**Catalytic Interaction Between Alkyl Dichloro Silanes and SOV/20-123-4-33/53  
Halogen Substitution Products of Benzene**

dependence of the yield of ethyl chloro-phenyl dichloro silane on the temperature of the synthesis. The following products are formed in the reaction of methyl dichloro silane: 6% remain unchanged; ~7% methyl dichloro silane, ~ 5% dimethyl dichloro silane, ~ 60% unchanged chloro benzene, ~ 4% intermediate fraction (boiling point 44-128°/29 mm), ~ 10% methyl chloro-phenyl dichloro silane, and ~ 5 % residue in the flask. Gaseous products contain 86.5-87.5% hydrogen, 9-10% methane, and 0.7-1% hydrogen chloride. The isomers of methyl chloro-phenyl dichloro silane are contained in the fractions as follows: ortho- ~20%, meta- ~ 45%, and para- ~ 35%. The total yield of all isomers amounts to 24-27% of the reacted methyl dichloro silane (the ratio of the isomers was determined by K. K. Pópkov). The yields were also given for other substances mentioned above. From table 2 it may be seen that in the said reaction the reactivity of the benzene nucleus decreases regularly with the successful substitution of a hydrogen atom by a halogen atom. This decrease is the more abrupt the higher the polarity of the halogen. There are 2 figures and 3

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Catalytic Interaction Between Alkyl Dichloro Silanes and SOV/20-123-4-33/53  
Halogen Substitution Products of Benzene

references, 1 of which is Soviet.

PRESENTED: July 14, 1958, by B. A. Kazanskiy, Academician

SUBMITTED: July 10, 1958

Card 3/3

KLEBANSKIY, A.L.; VOSIK, V.F.

Reactivity towards radicals of compounds used as models  
of the main types of synthetic rubbers. Part 1: Reaction  
with the tertiary butoxy radical. Vysokom.sped. 1 no.8:  
1242-1245 Ag '59. (MIRA 13:2)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka.  
(Butoxy group) (Rubber, Synthetic)

KLEBALSKIY, A.L.; VOSIK, V.F.

Reactivity toward free radicals of compounds modeling the  
basic types of synthetic rubbers. Part 2: Reaction with  
diphenylpicrylhydrazyl. *Vysokom.sped.* 1 no.8:1246-1248  
Ag '59. (MIRA 13:2)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteti-  
cheskogo kauchuka.  
(Rubber, Synthetic) (Hydrazyl)

KLEBANOV, A.; VOSEK, V.

Synthesis of the model compounds of the basic types of synthetic rubber structures and study of their reactivity with free radicals. In Russian. p.451

ACTA CHIMICA. (Magyar Tudományos Akademia) Budapest. Hungary  
Vol. 21, no. 1. 1959

Monthly list of East European Accessions (EEAI) 10 Vol. 2, no. 2, Feb. 1960  
level.

5 (3)  
AUTHORS:

SOV/79-29-3-16/61  
Garmonov, I. V., Klebanskiy, A. L., Chevychalova, K. K.

TITLE:

Preparation of Div inyl by the Catalytic Hydrogenation of Vinyl Acetylene (Izgotovleniye gidrirovaniye vinilatsetilena s tsel'yu polucheniya divinila). I. General Kinetic Rules of the Selective Hydrogenation of Vinyl Acetylene in Solution (I. Obshchiye kineticheskiye zakonomernosti izbiratel'nogo gidrirovaniya vinilatsetilena v rastvore)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 824-830 (USSR)

ABSTRACT:

The authors thoroughly investigated the catalytic hydrogenation of vinyl acetylene in order to increase the selectivity of this reaction and to find the technological basis of this process for its industrial utilization. On investigating the composition of the hydrogenation products of vinyl acetylene in the solution with various catalysts it could be found that the palladium catalyst produces the highest selectivity on the hydrogenation. This capability is illustrated by the following graduation order: palladium->iron skeleton->nickel skeleton->platinum black catalyst, which is in contrast with references 3 and 4. The hydrogenation with the palladium catalyst in the

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SOV/79-29-3-16/6

Preparation of Divinyl by the Catalytic Hydrogenation of Vinyl Acetylene  
I. General Kinetic Rules of the Selective Hydrogenation of Vinyl  
Acetylene in Solution

vapor phase at 130° was not possible owing to side reactions. Therefore the hydrogenation of vinyl acetylene was carried out on the palladium catalyst with finely powdered silica gel as carrier. It takes place in the first step of the process on vinyl acetylene and on hydrogen. In the kinetic range of hydrogenation the reaction rate is directly proportional to the quantity of the catalyst and does not depend on the intensity of stirring of the solution. In the diffusion range on the hydrogen the reaction rate increases proportionally to the increasing intensity of stirring of the solution and does not depend on the quantity of the catalyst. In both hydrogenation ranges the reaction rate increases proportionally to the increasing partial pressure of the hydrogen. In order to find out those conditions which produce the highest selectivity in the process and to facilitate the separation of the principal product of the reaction, the divinyl, (butadiene-1,3) in a pure state, the composition of the reaction products obtained at different intensity of hydrogenation was determined. In the initial stage of the process, up to a hydrogenation intensity

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SOV/79-29-3-16/61

Preparation of Divinyl by the Catalytic Hydrogenation of Vinyl Acetylene  
1. General Kinetic Rules of the Selective Hydrogenation of Vinyl  
Acetylene in Solution

~30% (calculated with respect to the acetylene bond) the affiliation of the hydrogen was found to take place mainly to the triple bond. On further hydrogenation in addition to this affiliation a hydrogenation of the divinyl being formed takes place wherein the reaction products represent a very complex mixture of hydrocarbons which are difficult to separate. By hydrogenation of the mixture of vinyl acetylene and divinyl the above mentioned reaction character was confirmed. On a low intensity of hydrogenation (up to 30%) practically only divinyl is obtained. There are 4 figures, 2 tables, and 9 references, 5 of which are Soviet.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka (All-Union Scientific Research Institute of Synthetic Rubber)

SUBMITTED: February 3, 1958  
Card 3/3



5 (3)  
AUTHORS:

Garmonov, I. V., Klebanskiy, A. L., Chevychalova, K. K. 507/79-29-3-17/61

TITLE:

Preparation of Divinyl by the Catalytic Hydrogenation of Vinyl Acetylene (Kataliticheskoye gidrirovaniye vinil-atsetilena s tsel'yu polucheniya divinila). I. Influence Exerted by Various Factors Upon Rate and Selective Behavior of Hydrogenation of Vinyl Acetylene (I. Vliyaniye razlichnykh faktorov na skorost' i izbiratel'nost' gidrirovaniya vinil-atsetilena)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 830-836 (USSR)

ABSTRACT:

In the present paper the authors present data on the influence exerted by the nature of the carrier and solvent, the reaction temperature and the intensity of the mixing of the solution upon the rate and the selective behavior of the hydrogenation of vinyl acetylene. In order to investigate the influence of the conditions at the preparation of the catalyst and that of the character of the carrier upon the rate and the selective behavior of this hydrogenation, experiments with palladium on silica gel, with barium sulfate and with polyvinyl alcohol were carried out. It was found that a modification of the preparation conditions of the catalyst and of the nature of the carrier

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SOV/79-29-3-17/61

Preparation of Divinyl by the Catalytic Hydrogenation of Vinyl Acetylene  
I. Influence Exerted by Various Factors Upon Rate and Selective  
Behavior of Hydrogenation of Vinyl Acetylene

influences the reaction rate, but that the selective behavior of hydrogenation is not markedly influenced by these modifications. The results obtained theoretically completely correspond with the publications available in this field (Ref 2). From among all factors investigated the intensity of the mixing of the solution and the percentage of the quantity of the medium exert a noticeable influence upon the selectivity of the reaction. At a low intensity the reaction did not proceed selectively. In the alcohol solution with the  $\text{pH} > 7$  the reaction proceeded more rapidly but with less selection than in acid and neutral medium. The determined hydrogenation character of the dissolved vinyl acetylene in the presence of the palladium catalyst as well as the determined dependence of the selective behavior of the process on the intensity of the mixing of the solution completely agree with the absorption theory concerning the catalytic hydrogenation (Ref 4). There are 1 figure, 5 tables, and 5 Soviet references.

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SOV/79-29-3-17/61

Preparation of Divinyl by the Catalytic Hydrogenation of Vinyl Acetylene  
I. Influence Exerted by Various Factors Upon Rate and Selective  
Behavior of Hydrogenation of Vinyl Acetylene

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo  
kauchuka (All-Union Scientific Research Institute of Synthetic  
Rubber)

SUBMITTED: February 3, 1958

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15.9210

75679  
SOV/80-32-10-28/51AUTHORS: Klebanskiy, A. L., Timofeyev, O. A.

TITLE: Emulsion Copolymerization of Hexafluorobutadiene With Diene Compounds. Communication II

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Vol 32, Nr 10, pp 2294-2299 (USSR)

ABSTRACT: The study deals with the comparison of the reactivity constants of solution copolymerization and emulsion copolymerization of chloroprene with hexafluorobutadiene, and with the characteristics of copolymers thus obtained. The experimental part was described previously by the authors (in this journal, 1959, Vol 32, Nr 9). Esteramine (ester of diethylaminoethanol and lauric acid) was found to be the most suitable emulsifying agent, at an optimum concentration of 5%. The rate of polymerization increased with the acidity of the water phase; the optimum value was pH = 3. The optimum ratio of the water phase of the monomer mixture was 2:1. Among copolymerization catalysts,  $K_2S_2O_8$  was the most effective. The rate of polymerization increased with catalyst concentration; it depended also on

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Emulsion Copolymerization of Hexafluorobutadiene  
With Diene Compounds. Communication II

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SOV/80-32-10-28/51

the initial ratio of the monomers. The reaction slowed down with the increasing hexafluorobutadiene content, and increased with rise in temperature. The polymerization constants of emulsion and solution copolymerization determined on the basis of experimental data had practically the same value; this confirmed the authors' assumption that these constants do not depend on the manner in which the copolymerization is conducted. It was also established that the tendency to the alternation of chloroprene and hexafluorobutadiene molecules in the copolymer, as well as the tendency of hexafluorobutadiene molecules to join together, increased with the concentration of hexafluorobutadiene in the initial monomer mixture. Copolymers of hexafluorobutadiene with fluoroprene, isoprene, and chloroprene vulcanized at a high rate. It would be of interest, therefore, to investigate the feasibility of vulcanizing fluorinated olefins by incorporation in the chain of small amounts of hexafluorobutadiene as vulcanization inducing agent. V. N. Kartsev and F. Ye. Berman cooperated in the preparation of copolymer samples. There are 10 figures and 3 references,

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Emulsion Copolymerization of Hexa-  
fluorobutadiene With Diene Compounds.  
Communication II

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1 U.S., and 3 Soviet. The U.S. reference is F. R. Mayo,  
Ch. Walling, Chem. Rev., 46, 2, 191 (1950).

SUBMITTED: August 9, 1958

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S/138/60/000/007/001/010  
A051/A029

AUTHORS: Klebanskiy, A.L., Kartsev, V.N., Fomina, L.P., Trenke, Yu.V.  
TITLE: The Effect of Admixtures Present in Chloroprene<sup>15</sup> on the Stability of Nairite  
PERIODICAL: Kauchuk i Rezina, 1960, No. 7, pp. 1-3

TEXT: In the present article the authors have submitted data collected from a study of the effect of monovinylacetylene, divinylacetylene and air oxygen admixtures on the properties of nairite. In addition to this, the effects of iron salts on the polymerization process conducted in an emulsion and on the aging process were determined for salt concentrations of 0.02 - 0.2%. Although the effect of admixtures such as those investigated in the initial chloroprene monomer were previously studied and found to have the most harmful effect on the properties of rubber, for polymers of chloroprene, however, obtained by the polymerization process in an emulsion, this aspect was not sufficiently clarified. The presence of 0.1 - 0.2% monovinylacetylene admixtures in chloroprene was investigated and found not to have any effect on the nairite properties in this concentration.

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S/138/60/000/007/001/010  
A051/A029

### The Effect of Admixtures Present in Chloroprene on the Stability of Nairite

tration. Larger amounts were not considered since they actually do not occur in the monomer (Fig. 1). As much as 0.05 - 0.2% of divinylacetylene in chloroprene decreases the plasticity of nairite and also decreases its stability during thermal aging (Fig. 2 and 3). The latter effect is explained: 1) by the participation of the admixtures in the process of copolymerization with the formation of ramified structures due to the multi-functional nature of these compounds; 2) by the activation of the oxidizing process, since it is known that the divinylacetylene admixtures activate the oxidizing processes of chloroprene with the oxygen from air. These data point to the necessity of purifying the monovinylacetylene admixtures. The stability of nairite is also lower when it is polymerized in an air medium, and it has a greater tendency to scorching, than when polymerized in a nitrogen medium (Fig. 4). Nairite is oxidized and forms active peroxides. The amount of saponifiable chlorine increases in proportion to the amount of oxygen absorbed. The increased quantity of the saponifiable chlorine causes the polymers to undergo structuralization when being stored or processed and also causes the premature vulcanization as a result of the interaction between the metal oxides

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S/138/60/000/007/001/010  
A051/A029

The Effect of Admixtures Present in Chloroprene on the Stability of Nairite during the processing. Finally, Figure 5 shows that the presence of a 0.02 - 0.2% concentration of iron salts in chloroprene does not affect the plasticity of nairite. There are 5 graphs.

ASSOCIATION: Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S.V. Lebedeva (The All-Union Scientific Research Institute of Synthetic Rubber im. S.V. Lebedev) ✓

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S/138/60/000/008/003/015  
AO51/A029

AUTHORS: Klebanskiy. A.L.; Fomina, L.P.; Kartsev, V.N.; Trenke, Yu.V.

TITLE: The Effect of Various Types of Stabilizers on the Change in Nairite Properties During Aging

PERIODICAL: Kauchuk i Rezina, 1960,<sup>4</sup><sub>A</sub> No. 8, pp. 9 - 13

TEXT: The authors studied the selection of more effective stabilizers of Nairite (chloroprene rubber) than those commonly used, such as thiuram E (2.5%) combined with neozone (an antioxidant, phenyl-beta-naphthylamine, 2%). Since the oxidizing effect of air on the stability of Nairite is considered one of the main factors during its storage and vulcanization for avoiding scorching especially at elevated temperatures, the proper selection of stabilizers acquires great significance. The effect of the above-mentioned commonly-used stabilizers was described in Refs. 2 and 3. These stabilizers, during longer storage periods at room temperature, as well as during the long-lasting processing of the mixtures at high temperatures (over 120°C), do not ensure a sufficient stabilizing effect of the Nairite: the plasticity of the standard rubber mixtures drops when these are heated for 1 hour. This drop in plasticity is assumed to be connected with the scorching effect of Nairite. In choosing the proper stabilizers, the structural charac-

S/138/60/000/008/003/015  
A051/A029

# The Effect of Various Types of Stabilizers on the Change in Nairite Properties During Aging

teristic of Nairite are considered, and thus the structuralizing features of the latter. It is deduced therefrom that in order to stabilize Nairite, a complex of substances must be used which is capable of preventing the oxidizing processes of the chloroprene, and bind the easily detachable hydrogen chloride. Two groups of compounds were investigated as anti-oxidants: phenyl- $\beta$ -naphthylamine derivatives (neozone D) and polyphenols. During the oxidation of the rubber molecule an inactive polymer molecule is formed as well as a neozone D radical, which is no longer capable of continuing the growth of the chain due to the stability. It is assumed that the anti-oxidizing effect of neozone could be increased by introducing polar substitutes (Cl, OH, etc) or substitutes containing conjugated systems of double bonds (Ref. 3). However, it was found in investigating other compounds, such as diphenylthiazine ( $C_6H_5NHC_6H_4$ ), phenylnaphthylthiazine ( $C_6H_5NHC_6H_4$ ), diphenylphenylenediamine ( $C_6H_5NHC_6H_4NHC_6H_5$ ), dinaphthylphenylenediamine ( $C_{10}H_7NHC_6H_4NHC_{10}H_7$ ), oxyneozone ( $C_{10}H_7NHC_6H_4OH$ ), that in the formation of radicals from these compounds less energy is spent, than from neozone D, and it is further assumed that these radicals formed would be more stable, and less given to a shift in

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A051/A029

### The Effect of Various Types of Stabilizers on the Change in Nairite Properties During Aging

the chains. Based on these assumptions, it is stated that the listed compounds would be better and more effective inhibitors of the oxidizing processes, than neozone D. The application of neozone D derivatives, with polar substitutes (oxy-group, sulfide bonds) as stabilizers, or increasing the degree of linkage (di-phenyl- and dinaphthylphenylenediamines), does not increase the stability of Nairite. It does, however, increase its tendency to scorching during thermal aging (120 hours at 70°C). From these observations it is concluded that the scorching mechanism of the chloroprene polymers is not dependent on the oxidizing processes, but is due rather to the radical decay of the molecules along the polysulfide bonds forming polymer radicals, which in the presence of thiuram and other compounds, recombine with their radicals. Further deliberation follows on the advantages of neozone as an oxidizing inhibitor. As to the polyphenols in the role of stabilizers, it was found that in testing compounds containing phenol and oxide groups (lignin, dimethylphenyl-n-cresol, paradi-tertiarybutyldioxyphenylene-sulfide), these also had a negative effect on the stability of Nairite, increasing the scorching tendencies (Fig. 3). The accelerating effect of the phenols in this connection is thought to be associated with the fact that in the presence of a

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